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MOLECULAR LASERS IN E-BEAM STABILIZED  
DISCHARGED

S. R. Byron. et al

Mathematical Sciences Northwest, Incorporated

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# ABSTRACT

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20. Abstract continued

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STABILIZED DISCHARGES

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Covering the Period  
15 May 1973 to 15 November 1973

By

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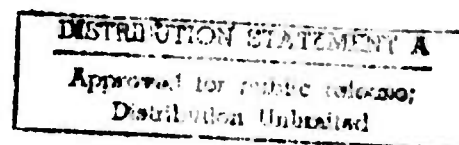
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## SECTION I

### SUMMARY

#### 1.1. HF and DF Laser Studies

During this reporting period, laser emission has been achieved in DF gas mixtures using electron impact excitation in e-beam stabilized electric discharges. Laser oscillation was observed in Ar/DF and Ar/D<sub>2</sub>/DF mixtures on the 2 → 1, 3 → 2, and 4 → 3 bands ranging in wavelength from 3.8 to 4.2 μm. The use of N<sub>2</sub> in the gas mixture eliminated laser emission from DF, contrary to the beneficial effect of N<sub>2</sub> on HF laser emission reported previously.

The use of helium rather than argon as a diluent in HF laser mixtures was found to produce higher laser cavity intensity at a given discharge current and voltage, indicating the possible beneficial effect of faster rotational equilibration. However, with helium as a diluent, the e-beam current required to achieve a given discharge current is significantly higher than that required when argon diluent is used.

Laser output energy was measured for several HF gas mixtures and yielded unexpectedly low results. The highest output energy obtained in a 30 μsec duration pulse was 11 millijoules and corresponded to only 0.06 percent efficiency and 0.3 J/l-atm. This laser output is one to two orders of magnitude less than expected on the basis of the computer model using currently available rate data. This result may be due either to the non-uniformities associated with the 5-tube plasma diode electron

gun or to a significant error in the kinetic modelling data now in general use. A uniform electron gun is being constructed, and probe laser measurements of gain and absorption have been started to provide further data for evaluation of the kinetic model.

The probe laser measurements, taken on several P-branch lines of the  $2 \rightarrow 1$  and  $3 \rightarrow 2$  bands of HF, showed first that there is no significant V-V exchange process between  $N_2$  and HF. Thus, the laser emission observed in Ar/ $N_2$ /HF mixtures arises wholly from electron impact excitation of HF. The apparent electron-energy-averaged cross-section for this process is about  $3 \times 10^{-17} \text{ cm}^2$ , which is comparable with the cross-section for  $H_2$  vibrational excitation. Additional probe laser data, obtained for Ar/ $H_2$ /HF mixtures, showed a very long decay time following termination of the discharge, and indicated the expected effect of V-V transfer from  $H_2$  to HF. However, a comparison with the results of kinetic model computations (which included direct electron impact excitation of HF) showed significant differences, both during the pulse and during the long duration decay. These measurements will be repeated in the uniform discharge chamber now being constructed.

### 1.2. Electronic State Lasers

Time resolved measurements of  $N_2$  first and second positive band emission in e-beam stabilized discharges showed evidence of three distinct excitation mechanisms. Direct excitation by the external e-beam current was seen, direct excitation by the electric discharge was observed, and

an indirect excitation process was seen which lasted several microseconds following termination of the applied discharge voltage. By analyzing the decay curves, the observed indirect excitation mechanism has been identified with the  $N_2(A)$  energy pooling process in which two  $N_2(A^3\Sigma_u^+)$  molecules collide to produce a molecule in a higher excited state, plus a ground state molecule.

The effect of  $SF_6$  and  $C_2H_6$  additives on the discharge properties and on the  $N_2$  fluorescence emission was also studied. The addition of 0.1 percent  $SF_6$  cut the discharge current by a factor of about 10, but permitted the application of a correspondingly higher value of  $E/N$ . This produced a higher rate of excitation of the C and B states by direct electric discharge processes, and resulted in a 10-fold increase in the ratio of the C state population to the B state population. The addition of  $C_2H_6$  was examined for its potential role as a catalyst to depopulate the vibrationally excited levels of the  $N_2(A^3\Sigma_u^+)$  state and thereby speed up the collisional quenching rate of the  $N_2(B^3\Pi_g)$  state. However, no change in the ratio of  $N_2(C)$  emission to  $N_2(B)$  emission was seen with the addition of  $C_2H_6$ . On the other hand, the indirect excitation mechanism for the B and C states decreased markedly with the addition of  $C_2H_6$ .

Laser cavity tests were conducted in  $N_2/Ar$  and  $N_2/He$  mixtures, with and without  $SF_6$  or  $C_2H_6$  additives, using mirror pairs coated for 3371 Å, 3650 Å, and 1  $\mu m$ , but with no success.

1.3. Uniformity of the 5-Tube Plasma Diode  
Electron Gun

The variation in electron beam current density through the foil for the 5-tube plasma diode was measured using an array of current probes. The ratio of the maximum current to the minimum current was found to be about 2, indicating the need for a more uniform electron gun.

## SECTION II

### HF AND DF LASER EXPERIMENTS

#### 2.1. Ar/DF and Ar/D<sub>2</sub>/DF Laser Cavity Measurements

Using the 5-tube plasma diode electron beam and electric discharge chamber described previously (Ref. 1), laser emission in Ar/DF and Ar/D<sub>2</sub>/DF was observed at wavelengths from 3.8 to 4.2  $\mu\text{m}$ . The experimental conditions were analogous to those found successful in producing HF laser emission in Ar/HF and Ar/H<sub>2</sub>/HF mixtures. The total gas pressure used was 200 torr, and the DF mole fraction was approximately 0.4 percent.

As with the Ar/HF laser, the value of E/N used in Ar/DF mixtures was only 0.1 to 0.2  $\times 10^{-16}$  V-cm<sup>2</sup> and the average discharge current density was about 4 A/cm<sup>2</sup>. The observed wavelengths and onset and termination times are given in Table I. The observed laser emission from Ar/DF provides further experimental confirmation of direct electron impact excitation of HF and DF vibration.

Laser emission was also observed in mixtures of Ar/D<sub>2</sub>/DF (92/7/0.4) using experimental conditions similar to those used previously for Ar/H<sub>2</sub>/HF (Ref. 1). The optimum E/N was 0.4  $\times 10^{-16}$  V-cm<sup>2</sup> and a maximum average discharge current of 12 A/cm<sup>2</sup> was used. The observed wavelengths and onset and termination times are given in Table I, along with prior results for HF gas mixtures. Typical oscilloscope traces of DF(3  $\rightarrow$  2) laser emission on several rotational lines are shown in Figure 1. It is apparent that maximum laser



Table 1. Time Resolved Spectroscopic Measurements of the Vibration Rotation Lines Observed in HF and DF Electric Discharge Lasers (Gas Pressure, 200 torr; time in  $\mu\text{sec}$  is given in parentheses).

Transition V	P(J)	Wavelength, $\mu\text{m}$		Gas Mixture			Wavelength, $\mu\text{m}$		Gas Mixture	
		HF		Ar/HF	Ar/H <sub>2</sub> /HF	Ar/N <sub>2</sub> /HF	N <sub>2</sub> /HF	DF	Ar/DF	Ar/D <sub>2</sub> /DF
1-0	9	2.823				(25-57)		-		
2-1	7	2.870		(10-32)		( 6-44)	(12-28)	-		
	8	2.911		(12-40)	(8 -22)	( 8-66)		-		
	9	2.954			(11-32)			3.837	(17-43)	
	10	2.999			(22-38)			3.876	(17-42)	
	13	-						3.999	(27-36)	
3-2	6	2.964		( 9-13)		( 6- 9)		-		
	7	3.005		(10-28)	(10-18)	( 7-45)		-		
	8	3.048			(10-27)	(32-48)		3.927	(15-24)	
	9	3.094			(24-32)			3.965	(15-46)	
	11	-						4.046	(15-30)	
	12	-						4.089	(20-36)	
	13	-						4.134	(32-38)	
4-3	10	-						4.141	(15-25)	
	11	-						4.184	(19-34)	

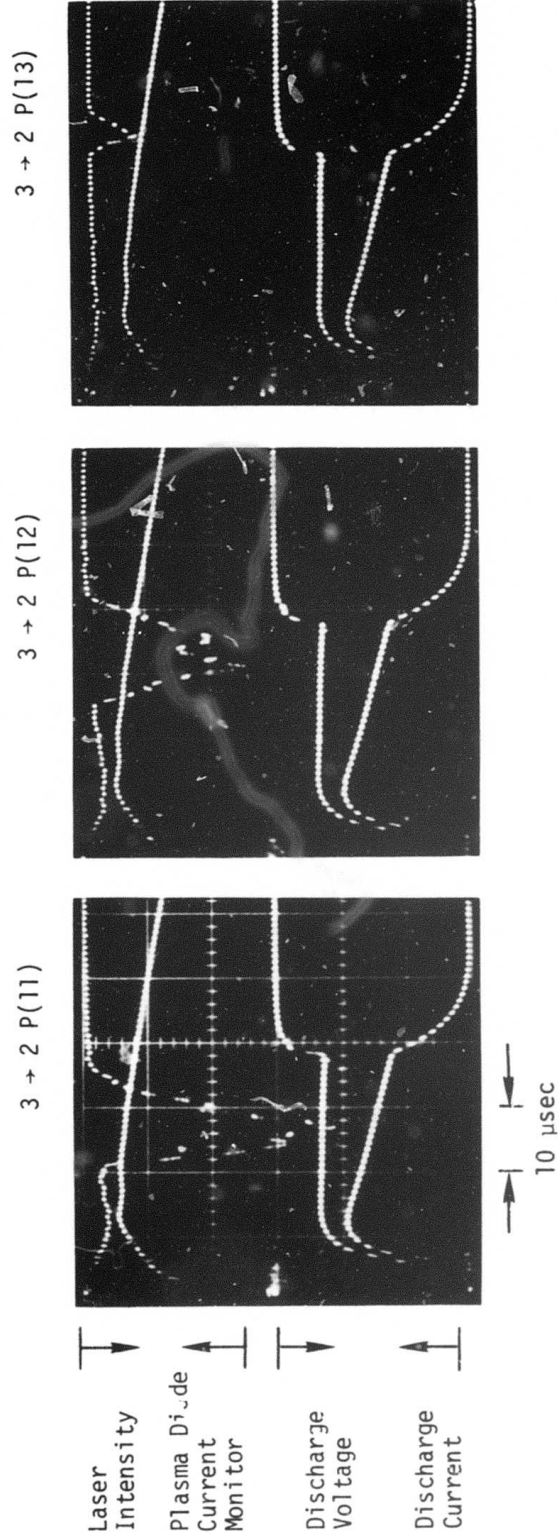


Figure 1. Time Sequence of Laser Emission from Ar/D<sub>2</sub>/DF Mixtures at 200 Torr. The Discharge Voltage Sensitivity is 700 V/Div and the Discharge Current Sensitivity is 1380 A/Div.

emission occurs sequentially at increasing J-values throughout the pulse. This observation indicates significant gas heating and partial equilibration of rotational populations by collisional processes. By contrast, the observed time sequence in Ar/N<sub>2</sub>/HF mixtures, illustrated in Figure 2, shows strong laser emission simultaneously on adjacent rotational lines, indicating considerably less collisional equilibration of HF rotation in the Ar/N<sub>2</sub>/HF mixture. The problem of rotational equilibration in HF laser mixtures is discussed further in Section 2.2 and in Section 3.

Addition of only 3 percent O<sub>2</sub> to an Ar/DF laser mixture completely quenched DF laser emission. When an 89/10/0.3 mixture of Ar/N<sub>2</sub>/DF was used, the HF isotopic impurity in the DF supply (about 10 percent) produced laser emission at 2.9 μm, but no laser emission from DF was found. These measurements confirm the detrimental role of O<sub>2</sub> and N<sub>2</sub> on the DF laser (due to rapid vibrational quenching of DF by O<sub>2</sub> and N<sub>2</sub>), and illustrate the importance of careful gas preparation and purification.

The DF laser emission observed in these experiments was achieved by eliminating the use of pre-mixed Ar/D<sub>2</sub> gas stored in conventional mild steel gas bottles. Flowmeters connected directly to the pre-purified argon and deuterium gas tanks by polyethylene tubing permitted mixing of the gases as they were flowing into the discharge chamber. This arrangement apparently yielded better gas purity than was achieved with the procedures used previously for pre-mixing Ar/D<sub>2</sub> samples.

## 2.2. Rotational Equilibration in HF Gas Mixtures

The effect of helium on the total HF laser intensity in a high-Q cavity is shown in Figures 3 and 4. As seen by comparing Figure 3(a)

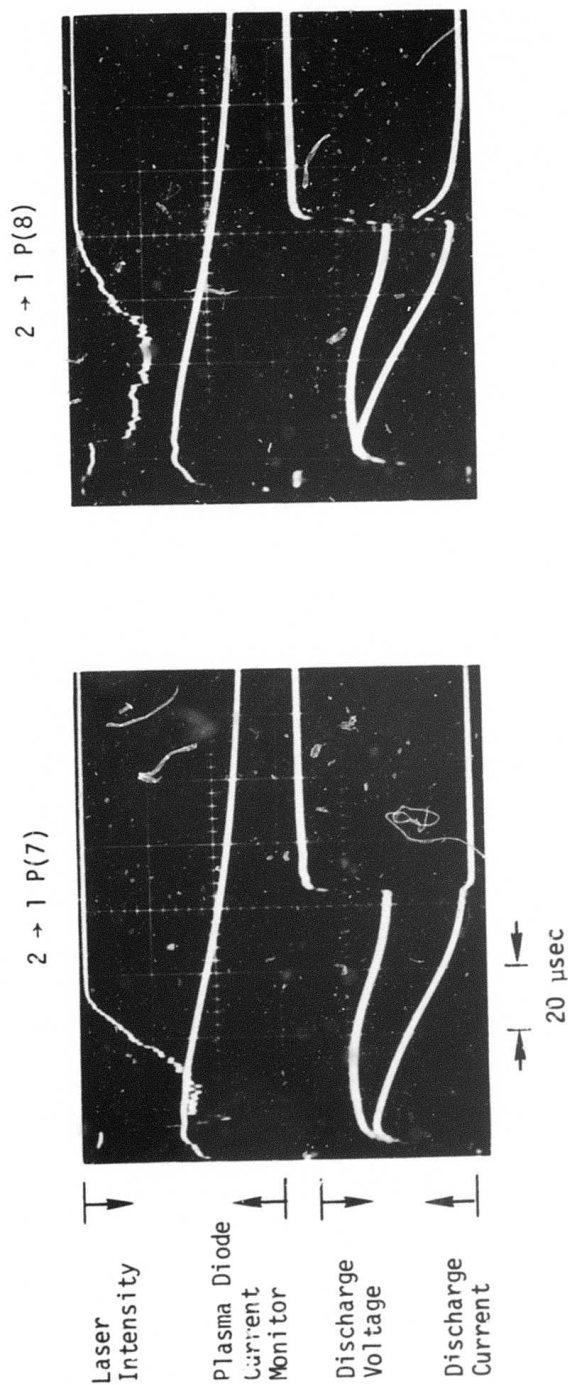


Figure 2. Time Sequence of Laser Emission from Ar/N<sub>2</sub>/HF Mixtures at 200 Torr. Voltage and Current Sensitivities Same as Figure 1.

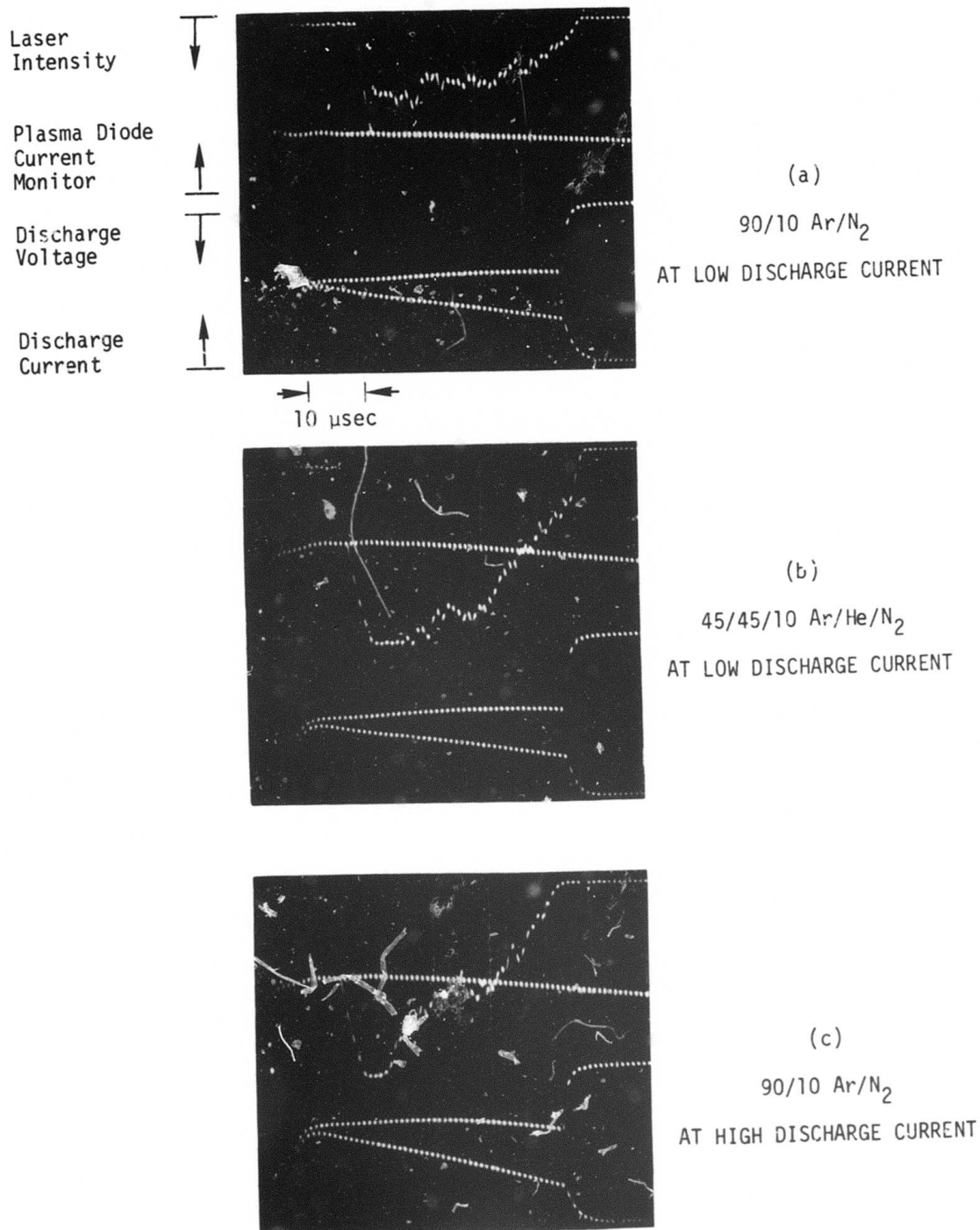


Figure 3. HF Laser Cavity Intensity in Ar/N<sub>2</sub> and Ar/He/N<sub>2</sub> Mixtures at 200 Torr, Using 0.4 Percent HF

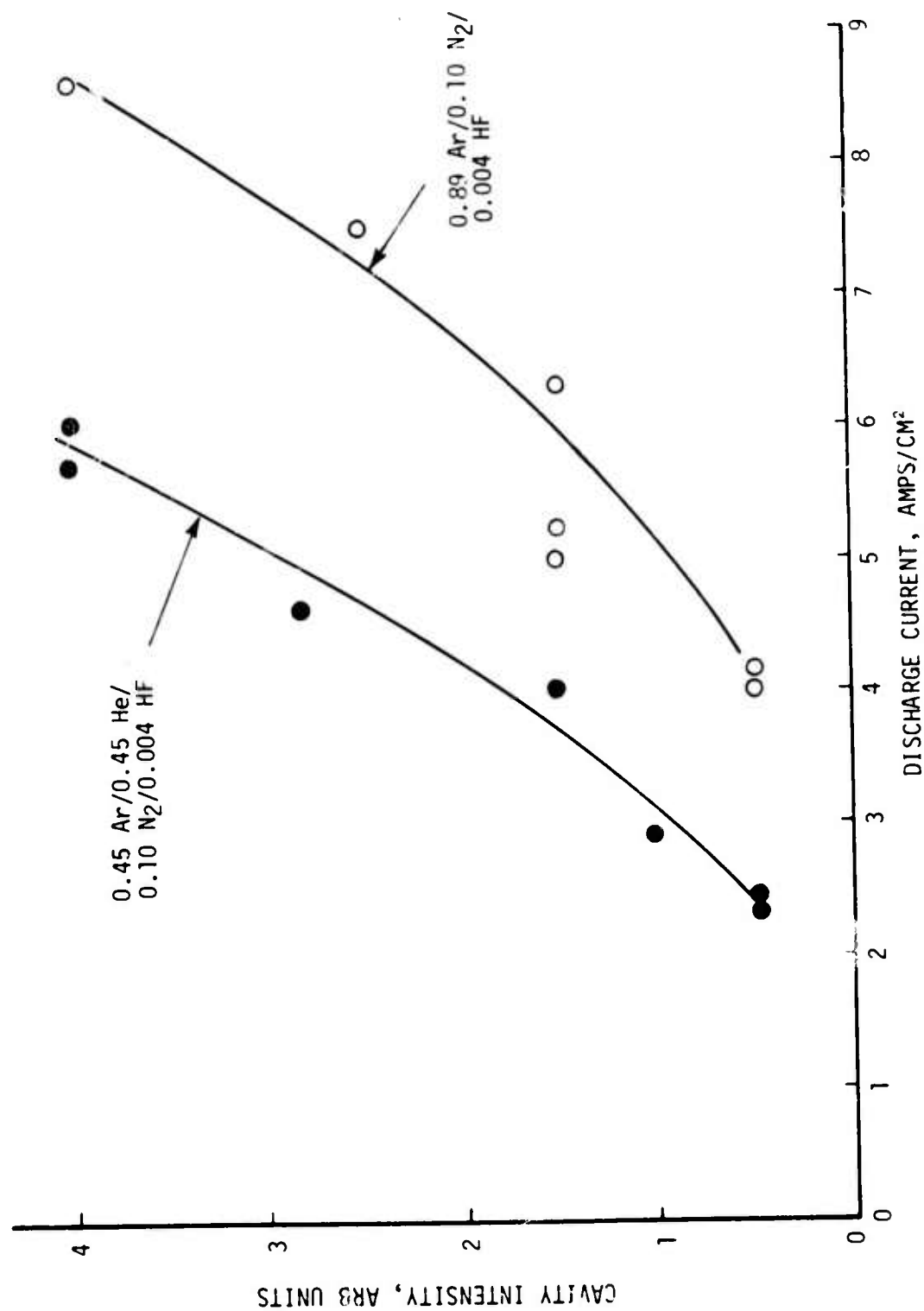


Figure 4. Peak Lase: Cavity Intensity in Ar/N<sub>2</sub>/HF and Ar/He/N<sub>2</sub>/HF Mixtures at 200 Torr, Using E/N Values of 0.7 to  $1.0 \times 10^{-16}$  V-cm<sup>2</sup>

with 3(b), the addition of helium increased the laser cavity intensity by about a factor of 4 for nearly equal values of  $E/N$  and discharge currents in  $\text{Ar/He/N}_2/\text{HF}$  mixtures compared to  $\text{Ar/N}_2/\text{HF}$ . The e-beam current was adjusted in order to produce equivalent discharge currents at fixed  $E/N$  for this comparison, since the added helium reduces the discharge current for a fixed e-beam current. When the e-beam current was not attenuated by running the plasma diode at low voltages and pressures, about the same cavity intensity was observed in  $\text{Ar/He/N}_2/\text{HF}$  and  $\text{Ar/N}_2/\text{HF}$  (compare Figures 2(b) and (c)). However, it is seen that the  $\text{Ar/N}_2/\text{HF}$  mixture required higher discharge current to achieve the same laser cavity intensity.

The increase in cavity intensity in mixtures containing helium is attributed to rotational relaxation of the HF by helium. Rotational heating of HF by V-R,T decay processes has been observed previously in measurements of vibrational decay of HF (Ref. 2). In those experiments, heavy dilution by argon was required to provide sufficiently rapid rotational relaxation during vibrational decay of HF. In our HF electric discharge laser strong rotational excitation of HF occurs through V-R,T decay and also by direct electron impact excitation of HF rotation. Thus the addition of helium can reduce the HF rotational temperature by increasing the rate of R-T relaxation. This lower rotational temperature would then increase the partial population inversion responsible for laser emission.

### 2.3. Laser Output Energy Measurements in HF Gas Mixtures

An optical output coupler was added to the high-Q laser cavity (Ref. 1) used in these experiments by introducing a  $\text{CaF}_2$  flat between one  $\text{CaF}_2$  Brewster angle window and one total reflector. The normal to the  $\text{CaF}_2$  output coupler was rotated at various angles in a plane containing the optical axis and the normal to the Brewster window. Thus the output coupling range is from zero at the Brewster angle to a maximum of 12.6 percent at near normal incidence (3.15 percent per surface per pass). With the output coupler at 45 degrees to the optical axis the output coupling is 3 percent, and with the normal at 30 degrees to the optical axis, it is 10 percent.

Output energy measurements were made for  $\text{Ar}/\text{N}_2/\text{HF}$  and  $\text{Ar}/\text{He}/\text{N}_2/\text{HF}$  mixtures using a "rat's-nest" energy meter (sensitivity 0.6 J/mV) having a collecting aperture of 2 cm diameter. For 10 percent output coupling, 11 millijoules output was measured for (89/10/0.3)  $\text{Ar}/\text{N}_2/\text{HF}$  at 200 torr. This corresponds to about 0.06 percent of the input discharge energy and an output energy density of about 0.3 J/l-atm. However, an  $\text{Ar}/\text{He}/\text{N}_2/\text{HF}$  (78/14/7/0.3) mixture under nearly identical e-beam current, discharge voltage, and output coupling gave approximately 65 percent of the output measured without helium. Hence, any effect helium may have on the rotational equilibration of HF (as noted in the previous section) is apparently offset by the reduced discharge current produced by the presence of large helium fractions and/or by an increase in the V-R,T decay of HF caused by the helium.



Laser output measurements were also made for Ar/H<sub>2</sub>/HF mixtures (94/5/0.4). Using the same output coupling (10 percent) and energy meter described above, only about 30 percent of the maximum energy measured for Ar/N<sub>2</sub>/HF mixtures was obtained. This reduced output energy may be due in part to the nonuniform electric discharge, which produces regions of absorption as well as regions of gain for Ar/H<sub>2</sub>/HF mixtures, as shown by the probe laser measurements described in Section III. To overcome the effects of non-uniformity, a uniform, 50 cm long, plasma diode electron beam is being constructed.

#### 2.4. Chemical Laser Output Observed with Ar/H<sub>2</sub>/SF<sub>6</sub> Mixtures

The laser wavelengths obtained from Ar/H<sub>2</sub>/SF<sub>6</sub> mixtures (87/10/3) using electron beam excitation were studied since this laser can be operated at the same pressure as the Ar/H<sub>2</sub>/HF and Ar/HF lasers and hence would be suitable for probe measurements free of pressure induced line shift problems. The large electron attachment cross section of SF<sub>6</sub> prevented any discharge current from being drawn when an external electric field was applied. Thus only electron beam excitation was used.

The observed lines, using the entire plasma diode are shown in Table II. A typical oscilloscope trace is shown in Figure 5, indicating long pulse laser emission at high pressure (200 torr), which would provide a useful probe laser. A single plasma diode tube was also used to give laser emission; the effective excitation path was only 8 cm.

Table II

Spectroscopic Measurements of Chemical Laser Emission in  
 $\text{Ar}/\text{H}_2/\text{SF}_6$  Mixtures  
 (Gas Pressure 200 Torr)

Transition V	P(J)	Wavelength, $\mu\text{m}$	Time Duration ( $\mu\text{sec}$ )
2-1	5	2.795	6-16
	6	2.832	13-42
3-2	5	2.926	7-23

LASER EMISSION

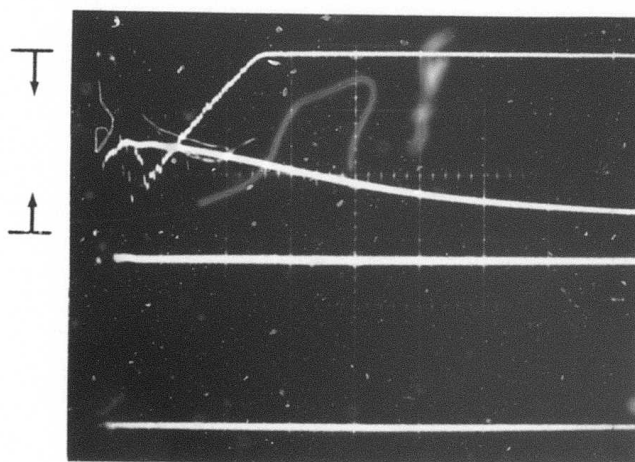
PLASMA DIODE  
CURRENT  
MONITOR

Figure 5. HF Laser Emission on All Lines from  $\text{Ar}/\text{H}_2/\text{SF}_6$  Gas Mixtures at 200 Torr Pumped Directly by External Electron Beam Excitation Alone (Time Scale - 20  $\mu\text{sec}/\text{div}$ )

Although the chemical laser lines noted in Table II are not the same as those observed in the HF electric discharge laser, it is very likely that a cavity with a grating could be used to select the desired lines, making this a useful probe laser for elevated pressure operation. The signal level from the chemical laser was not high, however, and the optical gain may be too low to accommodate the insertion loss introduced by the use of a grating in the cavity. This approach will be pursued further if it becomes necessary to develop a high pressure probe laser.

## SECTION III

## HF KINETICS MEASUREMENTS AND ANALYSIS

Time resolved probe laser measurements of HF gain and absorption were made to obtain information on the population of HF vibrational levels. This information was needed to verify the V-V pumping mechanism in the  $H_2$ /HF system and to determine the correct pumping mechanism in  $N_2$ /HF mixtures. Quantitative information on the V-V and V-R,T rate constants can be obtained by comparing these results with those obtained from the computer model being developed. The following section describes the experimental measurement of gain and absorption, summarizes the initial results that have been obtained and presents some comparisons with computer calculations.

### 3.1. HF Probe Laser Absorption Measurement Technique

A resistor loaded pin laser (Ref. 3) was used as a probe for the gain and absorption measurements. The pin discharge initiates the HF chemical laser by dissociation of  $SF_6$  which leads to reaction of F atoms with either  $H_2$  or  $CH_4$ . Figure 6 shows the optical arrangement used for these measurements. The teflon scatterer in front of the monochromator slit was used to eliminate probe laser beam deflection caused by the heated gases in the e-beam discharge chamber. The effect of this deflection was especially evident for Ar/ $H_2$ /HF mixtures, where rotational heating was significant and led to a time dependent index of refraction change in the gas, causing severe

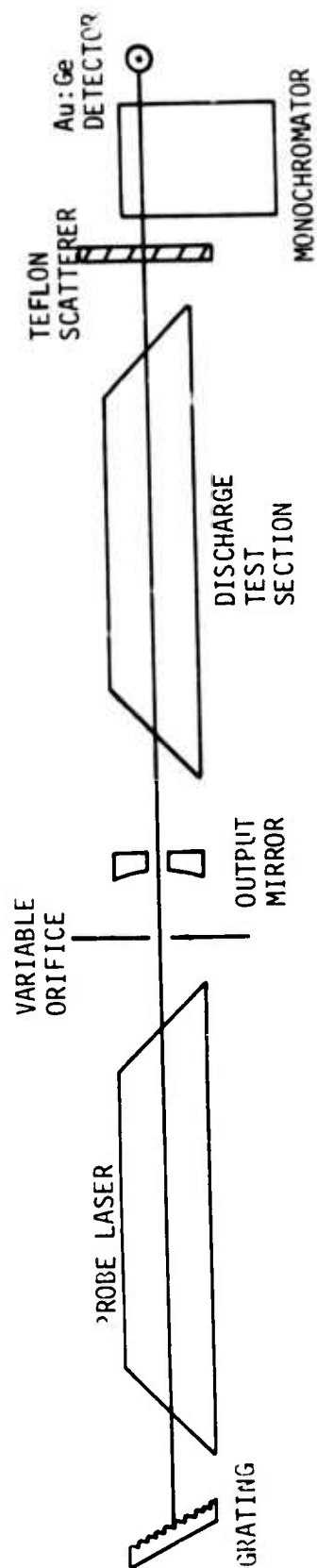


Figure 6. Optical Arrangement Used for HF Probe Laser Absorption and Gain Measurements

deflection of the probe laser beam. The teflon scatterer eliminated signal changes at the detector caused by refractive index changes in the gas, as verified by experiments in Ar/H<sub>2</sub> gas mixtures.

Since the probe laser pulse lasted only about 1  $\mu$ sec, a series of experiments at one operating condition was required to obtain the time history of the gain or absorption in the long pulse electric discharge laser. The accuracy of the measurement depended principally on the reproducibility of the peak intensity of the probe laser pulse. With a variable orifice aperture in the probe laser cavity to improve shot-to-shot reproducibility, the accuracy realized in these initial measurements was about 10 to 20 percent.

For line selection, a Bausch and Lomb 3.0  $\mu$ m blazed grating (Blaze Angle 26°45') was used in the probe laser cavity and a  $\frac{1}{4}$ -meter Jarrell-Ash monochromator was used just prior to the detector. The cavity grating alone was sufficient to isolate individual HF P-branch transitions on the 1-0, 2-1, and 3-2 bands. For convenience, the monochromator was left in the optical path for checking the wavelength calibration of the cavity grating.

HF concentrations in the test gas mixtures were measured using the P(7) 1-0 absorption line. Figure 7 shows the computed HF (1-0) transmission over the full 82 cm absorption path for different P-branch lines as a function of HF concentration. This measurement permitted reasonably accurate HF concentration determination even at values as low as 0.1 percent.

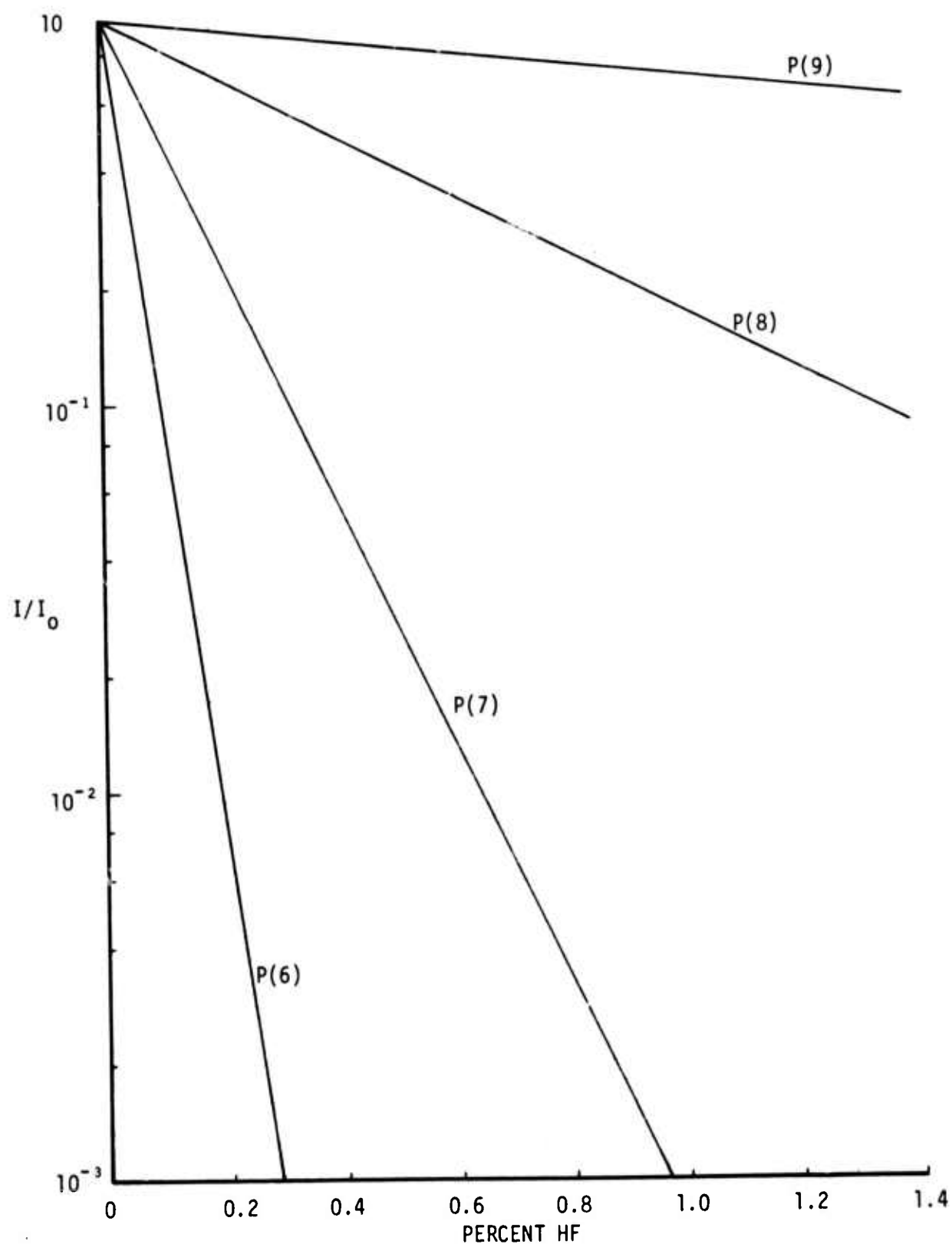


Figure 7. Calculation of HF( $v = 0 \rightarrow 1$ ) Transmission at 300°K and 200 Torr, Heavily Diluted with Ar, Over a Path Length of 82 cm

A serious difficulty, present in all of the absorption and gain measurements given here, is the magnitude of the pressure induced line shift of HF lines in the test gas mixtures relative to the probe laser line center. An approximation is made in all of the measurements discussed here that the shifted absorption coefficient is one-half that at line center in the high pressure test cell at 200 torr (this was discussed in the first semi-annual report (Ref. 4)). A more accurate measurement of this effect will be carried out when a high pressure probe laser is developed.

The probe laser could be fired at any desired time during or after the e-beam sustained discharge by a delay circuit. Typically five probe laser pulses were measured prior to a test; reproducibility of these traces was typically 15 percent. The buildup of gain or absorption was mapped by firing the 1  $\mu$ sec long probe laser once for each discharge pulse in the test gas, which required several oscillograms to be taken for an adequate time history.

### 3.2. Probe Laser Absorption Measurements of HF Vibrational Decay

Gain and absorption measurements were made during and after the discharge pulse in HF test gas mixtures. The decay rate following the pulse could be used to evaluate V-V and V-T processes. The populations of the upper HF levels could be used to evaluate the computer model being developed and to determine the temperature rise caused by the discharge.



To obtain vibrational decay rates, absorption measurements were made using the HF probe laser on 2-1 and 3-2 transitions at various time intervals following the crow-bar of the electric discharge. The electric discharge pulse duration was about 30  $\mu$ sec at current and voltage conditions comparable to those used to produce laser output as given in Section II. Decay rates of the  $v=1$  and 2 levels of HF were then calculated from the e folding time of the absorption decay as the vibrational energy of the gas mixture decayed. Table III summarizes the known HF V-V and V-T rates relevant to the systems investigated and will be referred to in the following discussion.

### 3.2.1. Ar/N<sub>2</sub>/HF Mixtures

The decay curve obtained for a 89/10/0.3 Ar/N<sub>2</sub>/HF mixture at 200 torr is shown in Figure 8. From this curve a decay time for HF( $v=1$ ) of 21  $\mu$ sec is obtained, which agrees very well with the V-T decay time calculated (20  $\mu$ sec) for this mixture using the data of Table III. The rapid decay of HF observed here clearly demonstrates that there is no significant two-quantum N<sub>2</sub> V-V transfer mechanism to pump HF( $v$ ) from N<sub>2</sub>( $v$ ) operating in the Ar/N<sub>2</sub>/HF electric discharge laser. Therefore the principal pumping mechanism for Ar/N<sub>2</sub>/HF mixtures is direct electron impact vibrational excitation of HF.

Table III  
Summary of H<sub>2</sub>/HF V-V and V-T Rate Data

Reaction	Rate Constant <sup>(a)</sup> (sec <sup>-1</sup> torr <sup>-1</sup> )	Reference
HF(1) + HF → 2HF(0)	8.7 × 10 <sup>4</sup> (b)	(5)
HF(1) + Ar → Ar + HF(0)	<60 (b)	(5)
HF(1) + H <sub>2</sub> $\xrightarrow{k_{12}}$ HF(0) + H <sub>2</sub>	$k_{21} + 2.6 k_{12} = 1 \times 10^3$ (b)	(6)
H <sub>2</sub> (1) + HF $\xrightarrow{k_{21}}$ H <sub>2</sub> (0) + HF		
H <sub>2</sub> (1) + H <sub>2</sub> → 2H <sub>2</sub> (0)	4.5 (b)	(7)
H <sub>2</sub> (1) + HF → HF(1) + H <sub>2</sub> (0)	6.3 × 10 <sup>4</sup> (c)	(5)
HF(2) + HF(0) → HF(1) + HF(1)	8 × 10 <sup>5</sup>	(8)
HF(3) + HF(0) → HF(2) + HF(1)	1.6 × 10 <sup>6</sup>	(8)
HF(4) + HF(0) → HF(3) + HF(1)	1.4 × 10 <sup>6</sup>	(8)
HF(1) + N <sub>2</sub> → HF(0) + N <sub>2</sub>	1.25 × 10 <sup>2</sup>	(5)

(a) Rate =  $K_{V-R,T} + K_{V-V}$  unless otherwise noted.

(b) Rate =  $K_{V-R,T}$

(c) Rate =  $K_{V-V}$

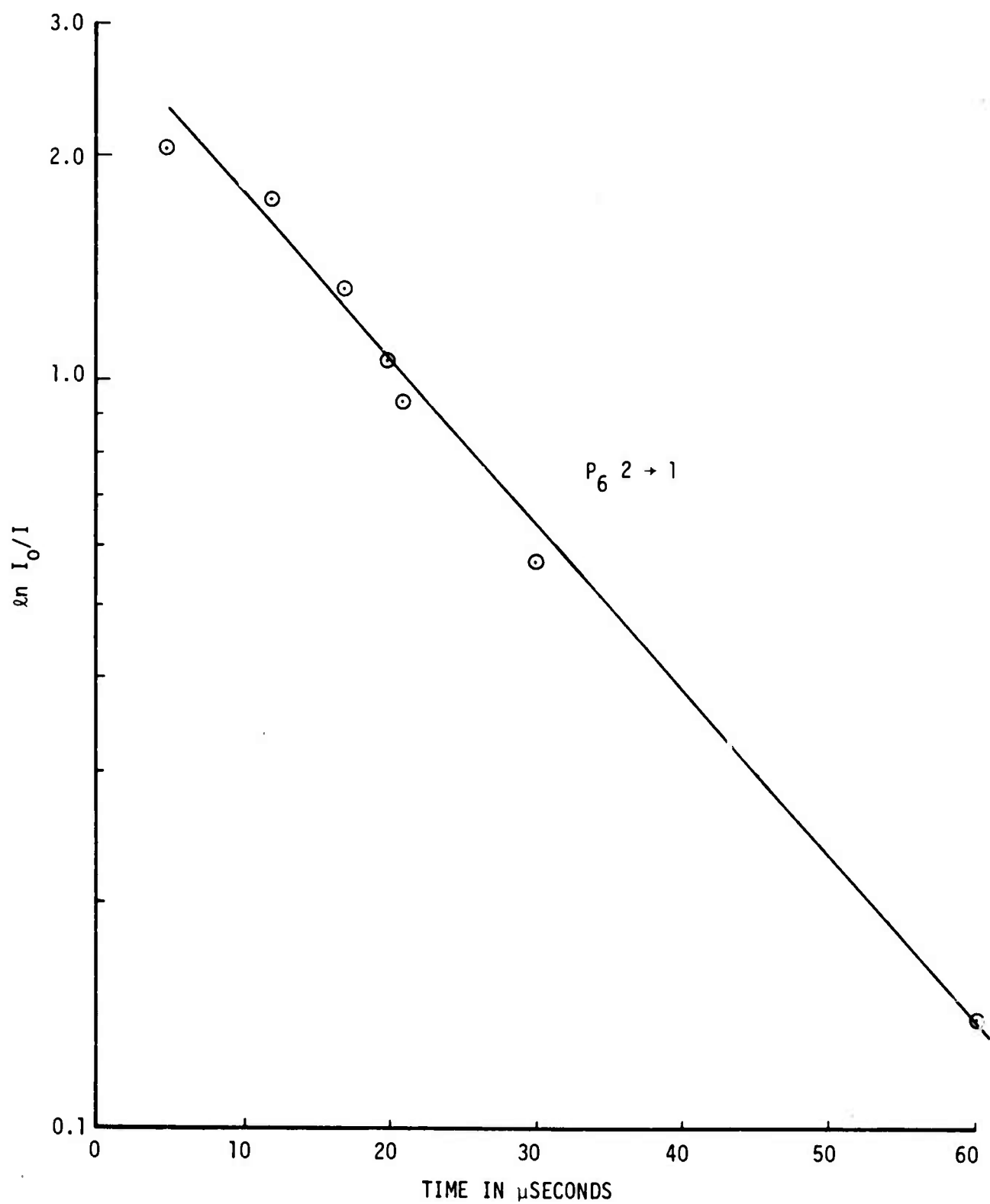


Figure 8. Probe Laser Absorption Measurements of HF( $v = 1$ ) Decay Following a 30  $\mu\text{sec}$  Electric Discharge Pulse in 89/10/0.3 Mixtures of Ar/N<sub>2</sub>/HF at 200 Torr

### 3.2.2. Ar/HF Mixtures

The decay curve obtained in a 99.8/0.2 Ar/HF mixture at 200 torr is shown in Figure 9. The short decay time (38  $\mu$ sec) for HF(v=1) is in agreement with the calculated decay time for this mixture using the rate constants given in Table III. Hence laser action observed for Ar/HF mixtures is due to electron impact pumping of HF, combined with VV ladder climbing as found in CO lasers. In contrast to CO systems, HF self V-R,T deactivation is extremely rapid, and electron attachment to HF is much larger than to CO. For these reasons large HF concentrations probably cannot be used for an efficient electrically excited HF laser system.

### 3.2.3. Ar/H<sub>2</sub>/HF Mixtures

In experiments performed with 89/10/0.3 Ar/H<sub>2</sub>/HF mixtures, the decay times are all greater than 100  $\mu$ sec. This verifies that the V-V transfer mechanism from H<sub>2</sub>(v) to HF(v) occurs in the H<sub>2</sub>/HF laser. Since the decay time is so long and involves the decay of the combined H<sub>2</sub> + HF vibrational energy, no simple numerical comparisons can be made. The complete computer model, described in more detail in Section 3.3, is required for evaluation and interpretation of these data.

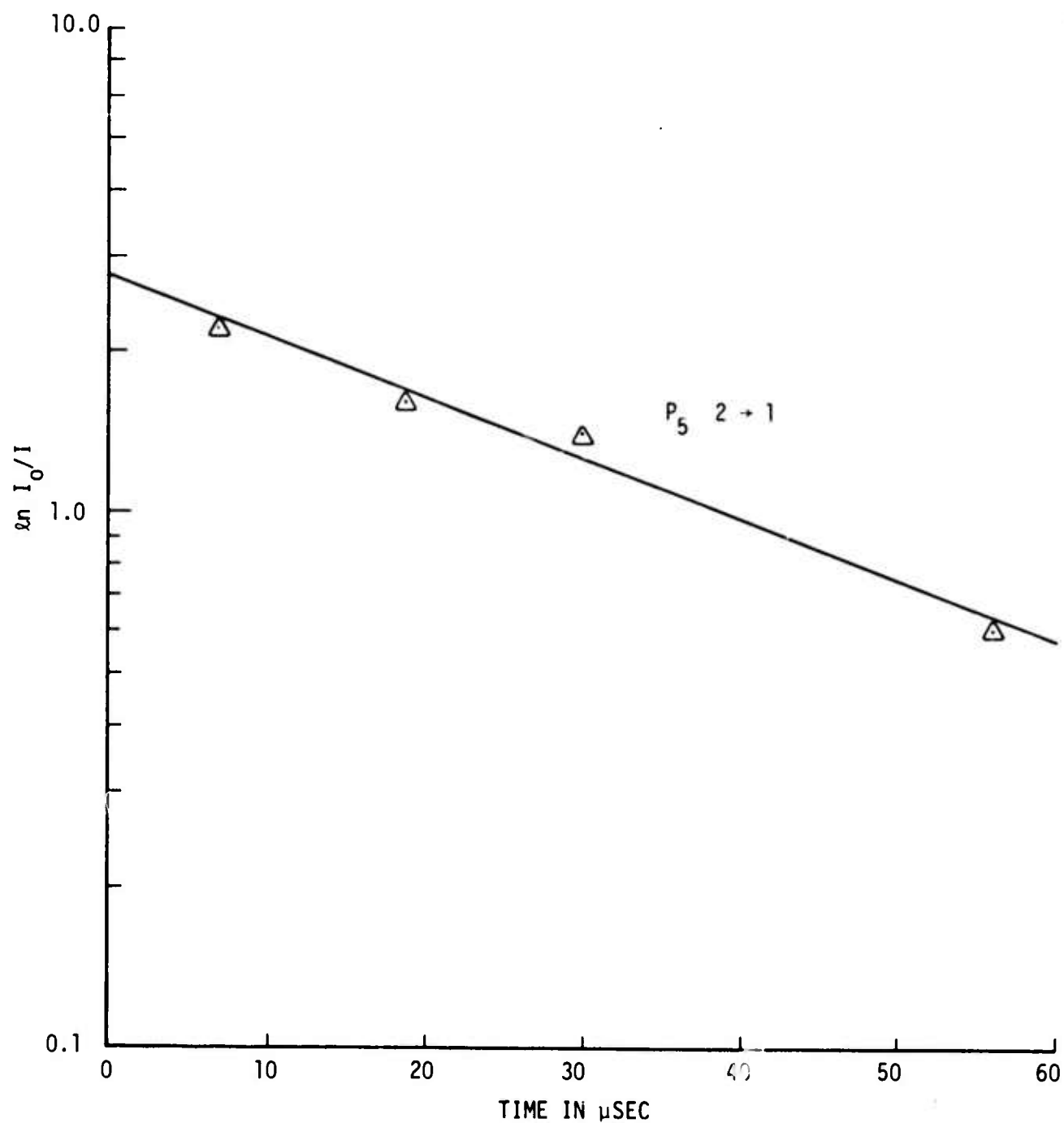


Figure 9. Probe Laser Absorption Measurements of HF( $v = 1$ ) Decay Following a 30  $\mu\text{sec}$  Electric Discharge Pulse in 99.8/0.2 Ar/HF Mixtures at 200 Torr

### 3.3. Comparison of Computer Model with HF Probe Laser Absorption Measurements

Interpretation of the vibrational decay observations in Ar/N<sub>2</sub>/HF and Ar/HF mixtures (Section 3.2) is relatively simple and does not require extensive computer modeling. However, interpretation of measurements of the HF vibrational level populations during the excitation pulse and the more complex decay in Ar/H<sub>2</sub>/HF mixtures can only be done with the aid of computer modeling. The major elements of the computer model have been described in previous Semi-Annual Reports (Refs. 1 and 4); the specific rate constants and other assumptions used in the present comparisons are given below. Comparisons are made with the results of absorption measurements on the P(5) through P(7) ( $v = 2 \rightarrow 1$ ) probe laser lines for Ar/N<sub>2</sub>/HF mixtures and on the P(5), P(6), P(7) ( $v = 2 \rightarrow 1$ ) and P(5) ( $v = 3 \rightarrow 2$ ) lines for Ar/H<sub>2</sub>/HF mixtures.

#### 3.3.1. Ar/N<sub>2</sub>/HF Excitation Processes

The vibrational decay measurements described in Section 3.2 indicated that the vibrational coupling between N<sub>2</sub>( $v$ ) and HF( $v$ ) is very weak. Thus the electric discharge excitation process occurs primarily through electron impact with HF( $v = 0$ ) to produce  $v = 1$  and possibly higher  $v$  levels. By carrying out probe laser absorption measurements on several  $v = 2 \rightarrow 1$  and  $3 \rightarrow 2$  transitions, the  $v = 1$  and  $v = 2$  populations were determined as a function of time (assuming the rotational temperature remains at 300 °K).

Experimental data are shown in Figure 10 for a 50  $\mu$ sec electric discharge pulse duration. It is interesting to note that the value of

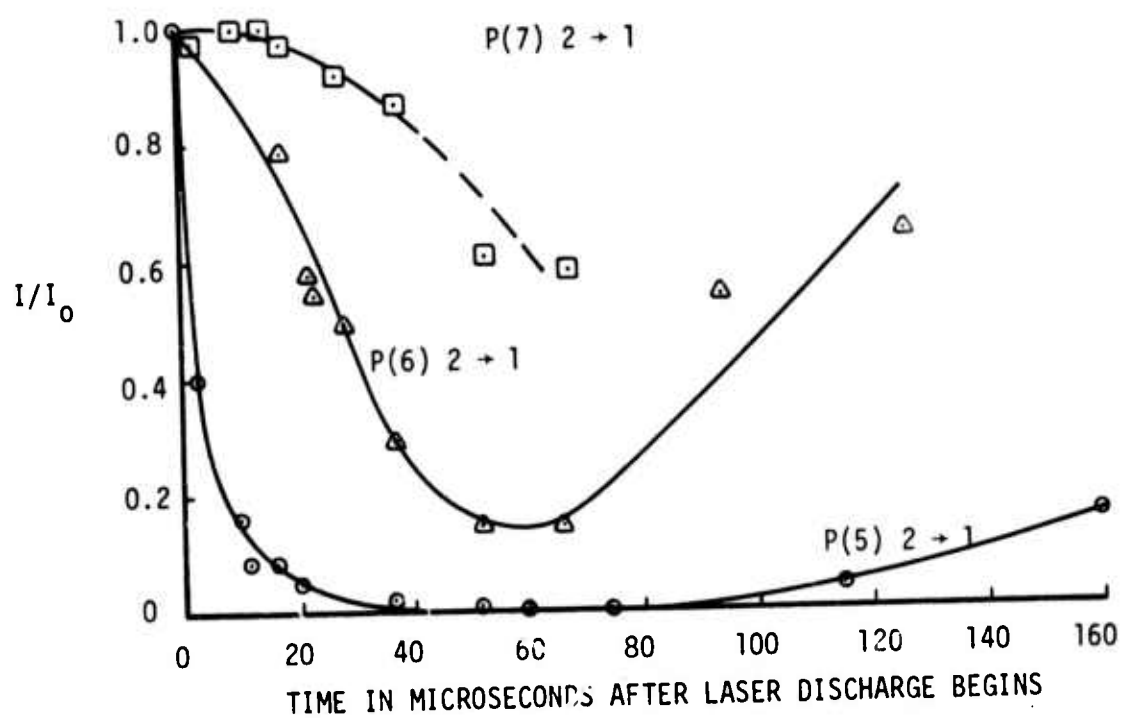
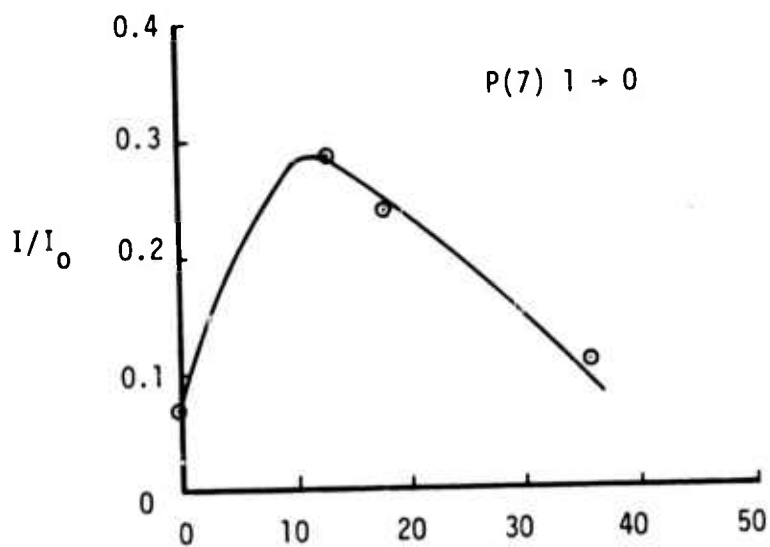


Figure 10. Probe Laser Measurements for a 50  $\mu$ sec Discharge Pulse in 89/10/0.4 Ar/N<sub>2</sub>/HF Mixtures at 200 Torr

the observed minimum in the  $P_7(0 \rightarrow 1)$  absorption at 13  $\mu\text{sec}$  is equal to the value computed on the basis that virtually all of the HF in the 50-cm long electric discharge region is removed by excitation, leaving only a 30-cm long residual absorption path.

Similar experimental data, using a 30  $\mu\text{sec}$  pulse duration, have been reduced to provide populations of the  $v = 1$  and  $v = 2$  levels, as shown in Figure 11. It is seen that the  $v = 1$  and  $v = 2$  populations rise together during the pulse, maintaining a ratio of about 3.7. From the initial slope of the  $v = 1$  population, an averaged cross-section for direct electron impact excitation of HF ( $v = 0$ ) to HF ( $v = 1$ ) can be estimated. The electron density is estimated to be  $1 \times 10^{13} \text{ cm}^{-3}$  on the basis of the measured electric discharge current density (8 amp/cm<sup>2</sup>) and an estimated drift velocity of  $5 \times 10^6 \text{ cm/sec}$ . An excitation cross-section of about  $3 \times 10^{-17} \text{ cm}^2$  is computed, assuming that the mean electron temperature is 1 eV and that the average is taken over the range of 0 to 2 eV. This value is comparable with the cross-section for electron impact vibrational excitation of  $\text{H}_2$  and may therefore play a significant role in the kinetics of Ar/ $\text{H}_2$ /HF mixtures.

Attempts to fit the results of Figures 10 and 11 using the present MSNW computer model for HF kinetics and the kinetic data of Table III have not yet yielded satisfactory agreement. However, the initial computations indicate some important trends. A simple model was assumed for the partitioning of electron pumping energy between HF and  $\text{N}_2$ , with  $\text{N}_2$  absorbing 96 percent and HF the remaining 4 percent. This 4 percent was partitioned on a trial basis between direct excitation of  $v = 1$  and  $v = 2$



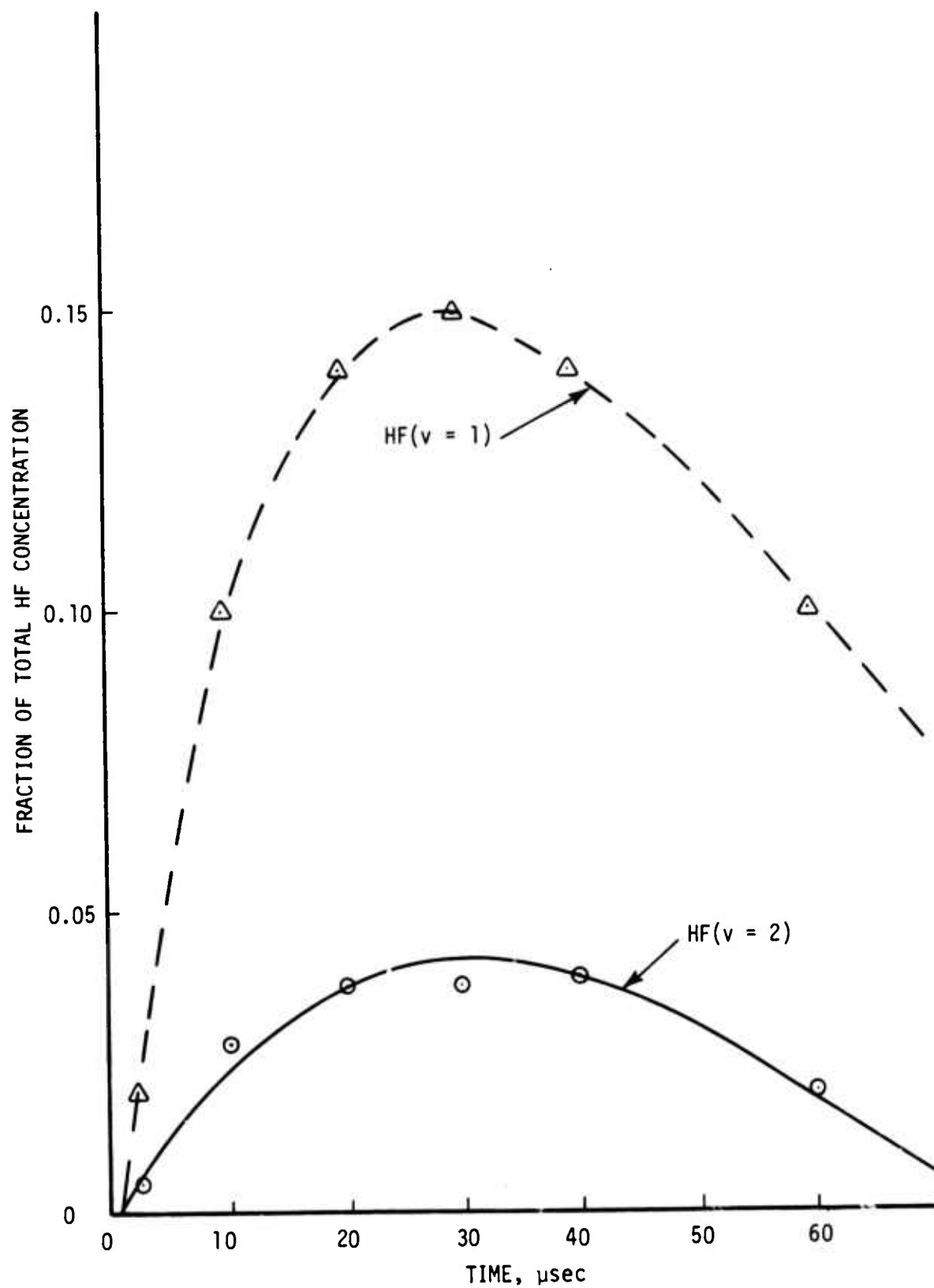


Figure 11. Measured HF Fraction in  $v = 1$  and  $v = 2$  in 89/10/0.4 Ar/N<sub>2</sub>/HF Mixtures at 200 Torr Obtained from Data of Figure 10

of HF. Vibrational energy transfer from  $N_2$  to HF was assumed insignificant. The HF rate data of Osgood, Sackett and Javan (Ref. 8), shown in Table III, were used for the upper ( $v = 2, 3, 4$ ) HF levels. However, these rates were taken as a sum of  $k_{VV}$  and  $k_{V-R,T}$ , rather than purely  $k_{VV}$ . Rates for the upper level V-R,T processes were then assumed to be equal to either  $vk_1$  or  $v^2k_1$ , where  $k_1$  is the HF ( $v = 1$ ) self V-R,T rate. The corrected V-V rates were obtained by subtracting  $vk_1$  or  $v^2k_1$  from the total rates of Reference 8. The V-V rates for levels  $v = 5, 6$  were taken as gas kinetic.

The computed gain or absorption of the  $2 \rightarrow 1$  P(7) transition is shown in Figure 12 for 3 specific cases. Referring back to Figure 10, we note that the measured gain or absorption on this transition was quite small throughout the first 20  $\mu$ sec of the pulse. This measured value differs from the computer model results that assume electron impact pumping only into the  $v = 1$  level, which show strong absorption at early times. By assuming that HF ( $v = 2$ ) is pumped at approximately the same power fraction as HF ( $v = 1$ ), the initial absorption is removed, but strong optical gain is predicted at later times during the pulse, which is not observed experimentally. This latter discrepancy may be due to the fact that very little gas heating was assumed in the computer model. Two conclusions are suggested:

- (1) direct electron impact pumping of both the  $v = 1$  and  $v = 2$  levels of HF is significant;
- (2) the HF V-V and V-R,T kinetics model does not describe these results satisfactorily.

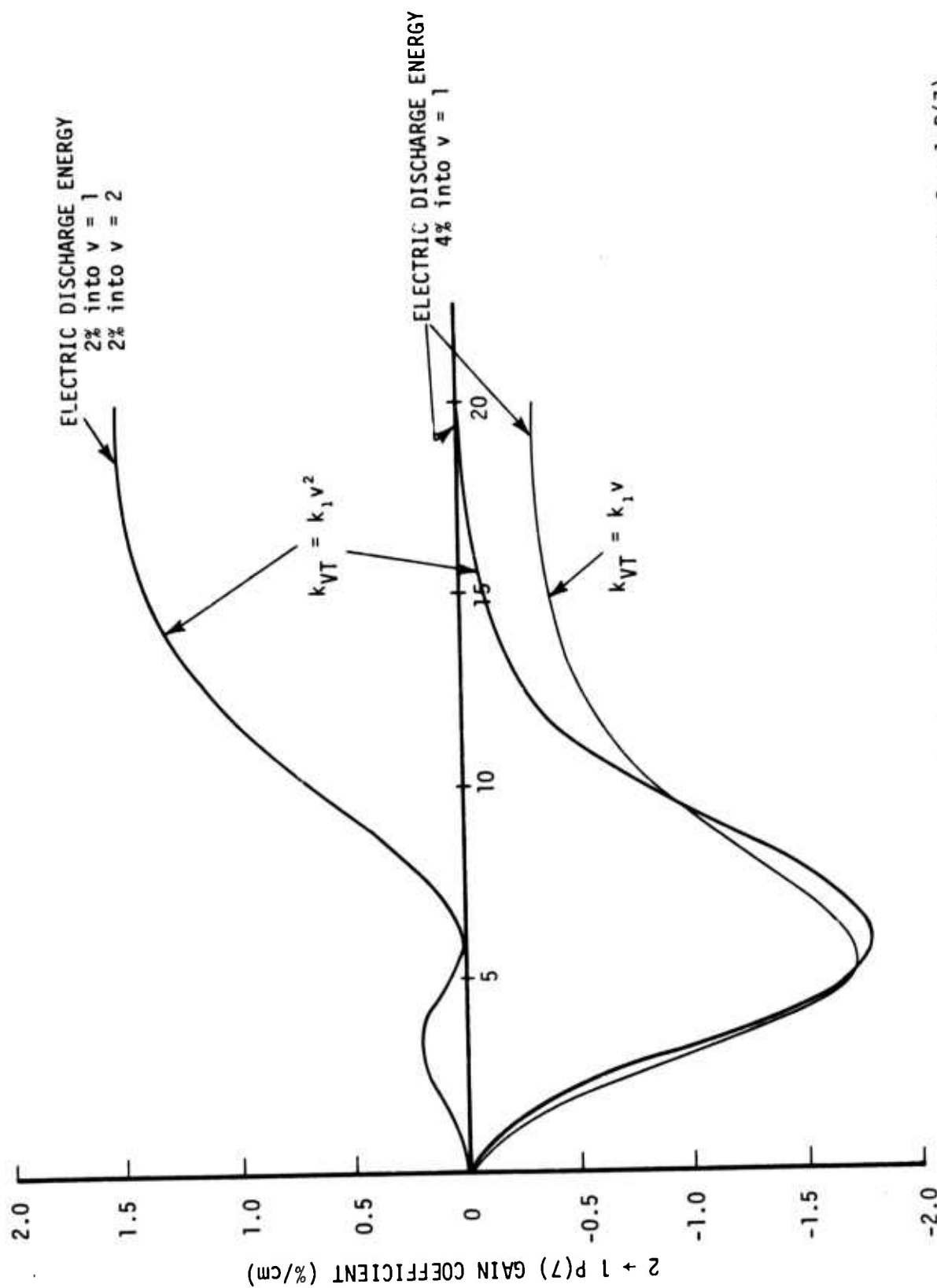


Figure 12. Computer Model Calculations of Optical Gain or Absorption on the  $2 \rightarrow 1 P(7)$  Transition of HF in 89/10/9.4 Mixtures of Ar/N<sub>2</sub>/HF at 200 Torr for a Power Input of 3 kW/cm<sup>3</sup>.

### 3.3.2. Comparison of Computer Model with Absorption Measurements in Ar/H<sub>2</sub>/HF Mixtures

Measurements of gain or absorption on the  $2 \rightarrow 1$  P(5), P(6) and P(7) and the  $3 \rightarrow 2$  P(5) transitions were made in 89/10/0.3 Ar/H<sub>2</sub>/HF mixtures at 200 torr using a 30  $\mu$ sec duration excitation pulse at a power input rate of 1.6 kW/cm<sup>3</sup>. The first set of experimental measurements is shown in Figure 13. Gain was not observed at any time on any of the lines studied. This result is consistent with the laser cavity tests made in the same mixture under the same conditions (Ref. 1), which showed no laser emission on the lines monitored in this set of tests.

The MSNW H<sub>2</sub>/HF kinetics model was applied to the conditions of these experiments in order to test the model. The basic kinetic information used in the code has been summarized in Table III. In addition, the effects of the following changes in parameters in the model were investigated:

- (1) the vibrational dependence of the V-R,T decay rate of HF due to HF collisions was varied as noted in Section 3.3.1;
- (2) the temperature dependence of the V-R,T decay rate of HF was included with a  $T^n$  law where  $n$  was varied between 0 and -2;
- (3) the V-V rate of H<sub>2</sub>( $v$ ) + H<sub>2</sub>( $v$ ) was varied both in magnitude and in the  $v$  dependence;
- (4) the V-V transfer rate from H<sub>2</sub>( $v$ ) to HF was varied both in magnitude and in the  $v$  dependence;
- (5) the direct electric discharge excitation rate of HF to produce  $v = 1$  and  $v = 2$  was varied;
- (6) the uppermost  $v$  levels ( $v = 6$ ) of H<sub>2</sub> and HF were assumed to be excited rapidly to higher levels.

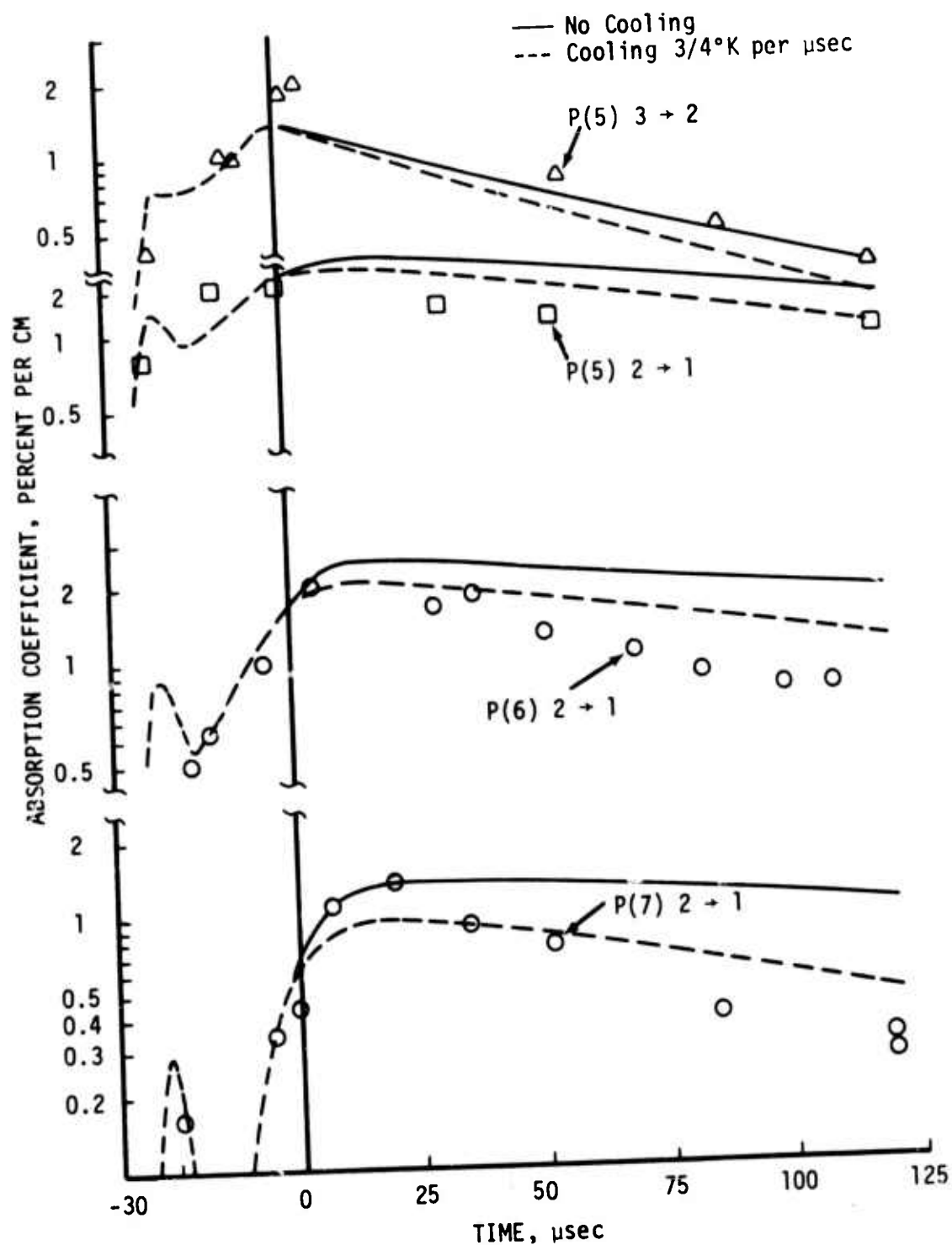


Figure 13. Comparison of Probe Laser Absorption Measurements with Computer Model Results in 89/10/0.3 Ar/H<sub>2</sub>/HF Mixtures at 200 Torr and a Power Input of 1.6 kW/cm<sup>2</sup> for 30 μsec

There was no single set of the adjustable parameters that provided a good fit to all of the data. One of the best fits obtained is shown as the solid curves in Figure 13. For this computation, the partitioning of electric discharge energy was the following:

$H_2(v = 1)$  excitation = 0.63

$H_2(\text{rot})$  excitation = 0.27

$HF(v = 1)$  excitation = 0.02

$HF(v = 2)$  excitation = 0.01

direct heating (elastic) = 0.07

In addition, the following kinetic model was used: the  $HF$  V-R, T decay rate by  $HF$  collisions was assumed proportional to  $v^2$ , with a  $T^{-1}$  dependence; the  $H_2$  V-V transfer rate among  $H_2$  molecules was based on a probability of 0.002 for  $v = 1$  and was assumed proportional to  $v$ ; and the  $H_2(v)$  transfer to  $HF(v)$  was assumed proportional to  $v$ .

It is seen in Figure 13 that there is general agreement between the computer model and the magnitude of the measured absorption coefficients; however, important details differ significantly. One of the principal differences is the discrepancy in rotational temperature during the excitation pulse. The  $2 \rightarrow 1$  P(7) line is predicted to go into optical gain midway in the excitation pulse, but this is not seen in the absorption measurements nor in the laser cavity measurements. The second principal discrepancy is in the decay following the discharge pulse. The results for  $2 \rightarrow 1$  P(5) and  $3 \rightarrow 2$  P(5) indicate that the computed decay rate is in fair agreement with experiment. However, the P(6) and P(7) lines of

$2 \rightarrow 1$  indicate a much faster decay than that predicted by the computer model. This suggests a faster cooling mechanism for the gas temperature or the rotational temperature than has been incorporated in the model. The addition of an artificial gas cooling rate (to model expansion cooling) at the rate of  $0.75^\circ\text{K}$  per  $\mu\text{sec}$  reduces the discrepancies somewhat as shown by the dashed curves of Figure 13. However, it is concluded that the computer model is not yet satisfactory, particularly in describing the rotational populations of HF. It appears likely that the rotational populations do not fit a Boltzmann distribution and that the transfer of rotational energy to translation is not as fast as assumed in the present model. This possibility is supported by the measured effect on laser output caused by replacing Ar with He, as discussed in Section 2.2.

## SECTION IV

ELECTRONIC STATE LASERS: FURTHER STUDY OF THE FIRST  
POSITIVE AND SECOND POSITIVE BAND SYSTEMS OF  $N_2$ 

The laser modeling studies described in our previous semiannual technical report suggested the following mechanisms for achieving a long pulse nitrogen laser: 1) pumping of the  $N_2$  (C and B) states by direct electron impact or  $Ar^*$  energy transfer; 2) pumping of the  $N_2$  (C) state and removal of the  $N_2$ (A) state using the energy pooling reaction ( $N_2(A) + N_2(A) \rightarrow N_2(C) + N_2(X)$ ); 3) selective collisional removal of the  $N_2$ (B) state (e.g., by  $C_2H_6$ ) to eliminate the self-terminating nature of the C  $\rightarrow$  B laser; and 4) use of small concentrations of electronegative molecules such as  $SF_6$  to increase the effective E/N by attaching low energy electrons and thus more effectively pump the  $N_2$  electronic states. These ideas have been tested experimentally during this reporting period and the results are discussed in the following text.

4.1. Experimental Set-Up

It was pointed out in the previous report that the onset of arcing prevented the achievement of the high E/N required for efficient pumping of the  $N_2$  electronic states. In an effort to alleviate the arcing, a new anode with a Rogowski profile at the edges was installed. In addition, the modular design of the e-beam apparatus results in non-uniformities in the discharge, as discussed in Appendix A. These non-uniformities will result in some variation in



the excited state population densities and could represent a serious loss due to absorption of the laser emission. An attempt to correct this problem was made by lowering the discharge screen 4 cm below the e-beam foil. Spreading of the electron beam due to scattering tends to make its profile more uniform at greater distances from the foil; however, the e-beam current density also decreases with distance from the foil, which results in lower discharge current densities.

The rest of the experimental set-up is identical to that used in the HF/DF experiments, with the exception of the mirror coatings and the ultraviolet detector. Gold mirrors were employed for the  $N_2$  first positive cavity tests, and two pairs of dielectric coated mirrors having maximum reflectivities of 99.9% at  $3370 \text{ \AA}$  and  $3650 \text{ \AA}$ , respectively, were used for the  $N_2$  second positive studies. Wavelength selection was obtained with a Jarrel-Ash 0.25 m Ebert Monochromator equipped with both  $6000 \text{ \AA}$  and  $2.1 \mu$  blazed gratings. The infrared emission was monitored with an Au:Ge detector while the ultraviolet emission was detected with an RCA 1P28 photomultiplier tube.

#### 4.2. Fluorescence Studies

Time resolved observations of the nitrogen  $C \rightarrow B$  and  $B \rightarrow A$  fluorescence indicate that the C and B states are formed by 1) direct electron impact and/or  $Ar^*$  excitation transfer, 2) metastable  $N_2(A)$  state self-collisions (energy pooling), and 3) electron impact on metastable  $N_2(A)$ . Experiments with no applied discharge voltage show

that the  $N_2$  (C and B) states are formed either directly by the e-beam itself, or by energy transfer from  $Ar^*$  produced by e-beam excitation. Figure 14(a) is a time history of the nitrogen  $C \rightarrow B$  and  $B \rightarrow A$  fluorescence produced by the e-beam only, while Figure 14(b) shows the effect on these emissions of applying a discharge voltage to the gas. The non-linear increase in both the  $3371 \text{ \AA}$  and  $1 \mu$  emission indicates that the C and B states are formed by some multi-step process, possibly by electron collisions with  $N_2(A)$ , by collisions between two A state molecules, or by electron impact with excited vibrational levels of ground state  $N_2$ .

Another important point to be noticed in Figure 14(b) is that the  $3371 \text{ \AA}$  emission decays with a time constant two orders of magnitude longer than the C state radiative lifetime ( $\sim 40 \text{ nsec}$ ). This observation suggests that the  $N_2(C)$  state is being produced from some long-lived excited species. The most likely candidates are excitation transfer from metastable Ar states or energy pooling by collisions of two metastable  $N_2(A)$  molecules. Transfer from metastable Ar atoms can be ruled out on the basis of the measured deactivation rate of  $Ar^*$  by  $N_2$ . The rate coefficient is  $3 \times 10^{-11} \text{ cm}^3/\text{sec}$  (Reference 9) which, for 20 torr of  $N_2$ , implies a transfer time of 50 nsec and an  $Ar^*$  decay time of 500 nsec. This is an order of magnitude shorter than the observed decay time.

Whether or not  $N_2(A)$  energy pooling is indeed responsible for the formation of  $N_2(C)$  should be apparent from the form of the second positive emission decay curve. Loss of the  $N_2(A)$  state is controlled by the energy pooling reaction until its population decays sufficiently that quenching predominates. Thus, if the energy pooling

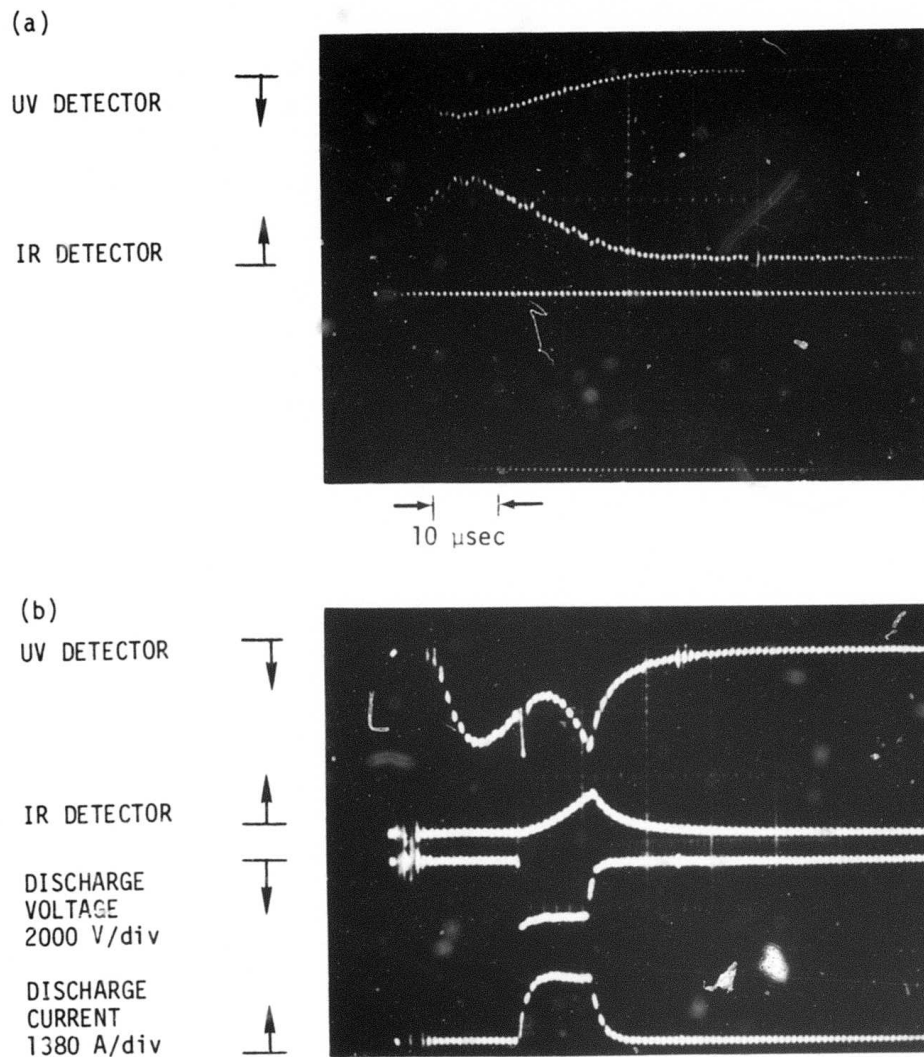


Figure 14. Time History of the Nitrogen  $C \rightarrow B$  ( $3370 \text{ \AA}$ ) and  $B \rightarrow A$  ( $1.04 \text{ }\mu\text{m}$ ) Fluorescence Produced a) by the E-Beam and b) by the E-Beam Stabilized Electric Discharge in an Ar/15%  $\text{N}_2$  Mixture at 200 Torr Total Pressure.

reaction which depends quadratically on the A state concentration, is the source of the C state, the 3371 Å emission will exhibit a non-exponential decay. In Figure 15, the intensity of the 3371 Å and 1 μ emission is shown as a function of time after the discharge crowbar. At early times (< 10 μsec) the decay is clearly non-exponential, but at later times it becomes exponential when quenching is the dominant loss process. The similarity between the B and C state decays indicates that there is a close relationship between their populations; the B state is either formed predominantly by radiative cascading from the C state, or it is also formed by A state self-collisions.

If the decay of the  $N_2(A)$  state is controlled by self collisions, then it can be described by a differential equation of the form

$$\frac{dA}{dt} = -QA + k_p A^2$$

Here Q is an apparent A state quenching rate constant and  $k_p$  is the A state self-annihilation rate coefficient.

The general solution of this differential equation is

$$A = \exp(-Qt) \left[ \left( \frac{1}{A_0} + \frac{k_p}{Q} \right) - \frac{k_p}{Q} \exp(-Qt) \right]^{-1}$$

where  $A_0$  is the concentration of  $N_2(A)$  at time  $t = 0$ . At early times ( $Qt \ll 1$ ) this solution has the asymptotic form

$$A^{-1} \sim A_0^{-1} + k_p t$$

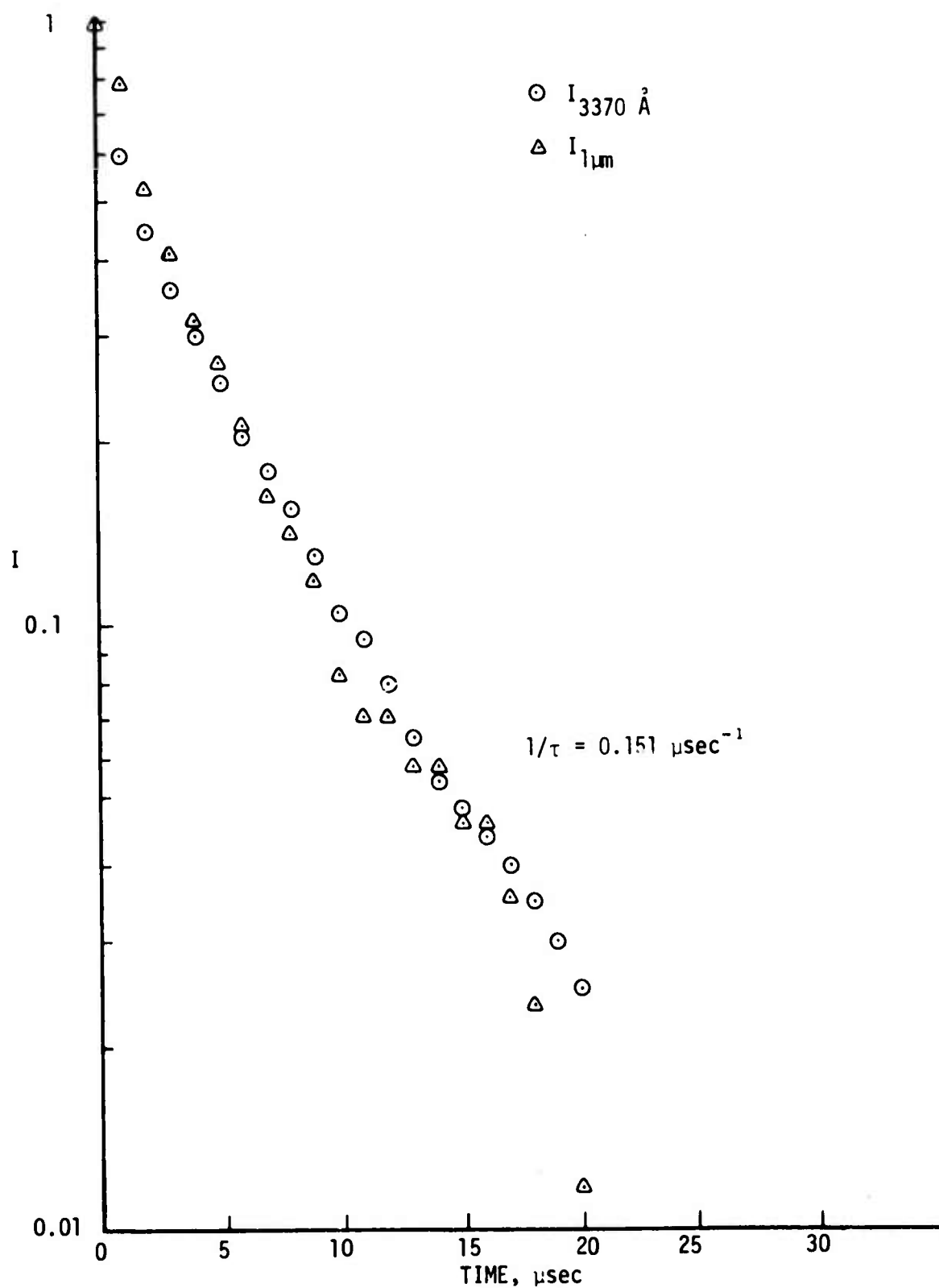


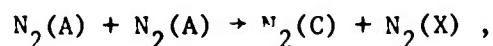
Figure 15. Time Decay of the 3370 Å and 1  $\mu$  Emission After the Discharge is Terminated for an Ar/15% N<sub>2</sub> Mixture at 200 Torr Total Pressure

and at late times ( $Qt \gg 1$ )

$$A \sim \exp(-Qt) \left( \frac{k_p}{Q} + \frac{1}{A_0} \right)^{-1}$$

Thus at short times, a plot of  $A^{-1}$  vs  $t$  should yield a straight line.

If the C state is formed from the reaction



then since the C state radiative lifetime is much shorter than its production time, the  $N_2(C)$  population should be proportional to  $[N_2(A)]^2$

and should have a decay rate equal to twice that of the A state. Hence at short times a plot of  $C^{-1/2}$  vs  $t$  should also yield a straight line.

Figure 16 shows the data of Figure 15 plotted as  $I^{-1/2}$  vs  $t$ . The linear relationship exhibited by both the C and B state emission implies that the A state decay is indeed being controlled by the energy pooling reaction, and that the energy pooling reaction is the source of the C and B state populations.

From the slope of the exponential decay of  $C^{1/2}$  at long times, it should be possible to estimate the A state quenching constant  $Q$ . Since the measured slope scales approximately with the  $N_2$  mole fraction, the A state quenching is more likely attributable to  $N_2$  itself or to some impurity present in or made from  $N_2$  than to Ar or to cold electrons. If the quenching is attributed to  $N_2$  then an approximate rate constant of  $8 \times 10^{-14}$   $\text{cm}^3/\text{sec}$  is derived from the late time decay of Figure 16. Since the reported values for the quenching coefficient of  $N_2(A)$  by

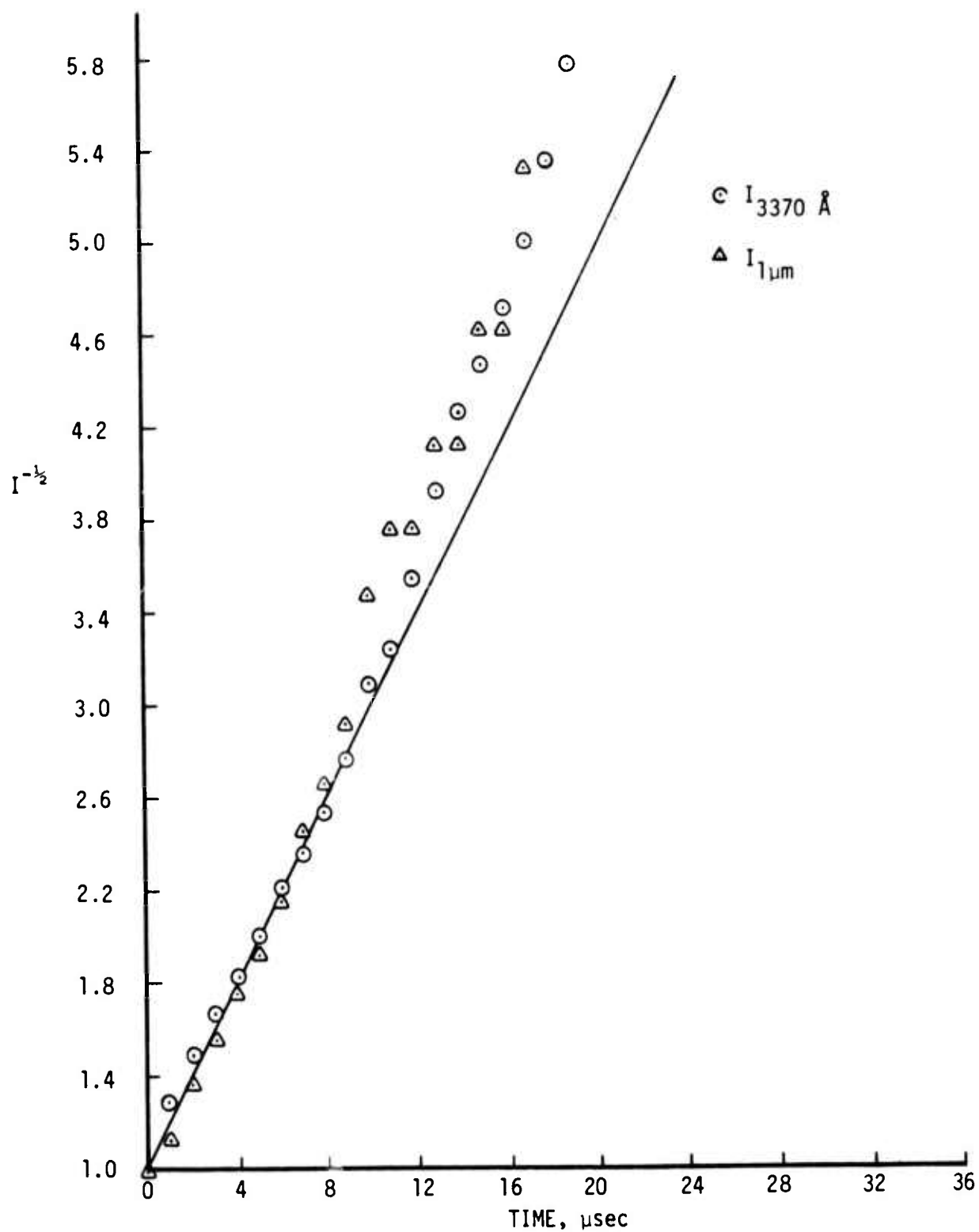
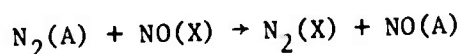


Figure 16. Plot of the Reciprocal of the Square Root of the  $\text{N}_2$  First and Second Positive Intensities Versus Time After the Discharge Crowbar

ground state  $N_2$  are  $\sim 10^{-16} \text{ cm}^3/\text{sec}$  or smaller (Ref. 10), the A state decay is probably due to an impurity either in the original  $N_2$  storage tank or one produced from  $N_2$  in the discharge. Assuming that it has a gas kinetic quenching cross section for  $N_2(A)$ , the impurity would constitute  $\sim 0.01\%$  of the gas mixture or  $0.1\%$  of the nitrogen gas itself.

In a study of Ar/ $N_2$  mixtures excited by a short duration, high-current density pulse of high energy electrons, Eckstrom et al., have obtained similar results for the decay of the  $N_2$  first and second positive emission (Ref. 11). By utilizing the nearly resonant energy transfer reaction



and monitoring the  $NO(A \rightarrow X)$  emission they confirmed that there is a close connection between the  $N_2(C)$  state and  $N_2(A)$  state decays and that at high  $N_2(A)$  concentrations self collisions control the decay of the A state population.

Recent rate data indicate that the energy pooling reaction forms the B state approximately four times faster than it forms the C state (Ref. 12). Thus, a  $C \rightarrow B$  laser relying on the energy pooling reaction as the pumping mechanism would be very inefficient. The rate coefficients for the energy pooling reactions as well as for other reactions pertaining to the nitrogen A, B, and C states are listed in Table IV.

It can be seen from the data of Table IV that excitation transfer from metastable  $Ar(^3P_{0,2})$  states produces the nitrogen B state 6 times faster than the C state. However, this ratio pertains to the overall



Table IV  
Ar + N<sub>2</sub> Excited State Reactions

NO.	REACTION	RATE COEFFICIENT (cm <sup>3</sup> /sec)	REFERENCE
<u>EXCITED STATE PRODUCTION</u>			
1.	Ar( <sup>3</sup> P <sub>2</sub> ) + N <sub>2</sub> → Ar + N <sub>2</sub> <sup>*</sup>	3 × 10 <sup>-11</sup>	9
2.	Ar( <sup>3</sup> P <sub>2</sub> ) + N <sub>2</sub> → Ar + N <sub>2</sub> (C)	1.2 × 10 <sup>-13</sup>	13
3.	Ar( <sup>3</sup> P <sub>2</sub> ) + N <sub>2</sub> → Ar + N <sub>2</sub> (B)	7 × 10 <sup>-13</sup>	14
4.	N <sub>2</sub> (A) + N <sub>2</sub> (A) → N <sub>2</sub> (C) + N <sub>2</sub> (X)	2.1 × 10 <sup>-11</sup>	15
		2.6 × 10 <sup>-10</sup>	12
5.	N <sub>2</sub> (A) + N <sub>2</sub> (A) → N <sub>2</sub> (B) + N <sub>2</sub> (X)	1.1 × 10 <sup>-9</sup>	12
6.	N <sub>2</sub> (A) + N <sub>2</sub> (A) → N <sub>2</sub> <sup>*</sup> + N <sub>2</sub> (X)	1.4 × 10 <sup>-9</sup>	12
<u>EXCITED STATE QUENCHING</u>			
7.	N <sub>2</sub> (C) <sub>v=0</sub> + N <sub>2</sub> → N <sub>2</sub> (?) + N <sub>2</sub>	1.1 × 10 <sup>-11</sup>	16
8.	N <sub>2</sub> (C) <sub>v=1</sub> + N <sub>2</sub> → N <sub>2</sub> (?) + N <sub>2</sub>	2.7 × 10 <sup>-11</sup>	16
9.	N <sub>2</sub> (B) + Ar → N <sub>2</sub> (A) + N <sub>2</sub>	1.6 × 10 <sup>-12</sup>	10
10.	N <sub>2</sub> (B) <sub>v=0</sub> + N <sub>2</sub> → N <sub>2</sub> (A) + N <sub>2</sub>	1.6 × 10 <sup>-12</sup>	17
11.	N <sub>2</sub> (B) <sub>v=1</sub> + N <sub>2</sub> → N <sub>2</sub> (?) + N <sub>2</sub>	2.2 × 10 <sup>-12</sup>	17
12.	N <sub>2</sub> (B) <sub>v=2</sub> + N <sub>2</sub> → N <sub>2</sub> (?) + N <sub>2</sub>	3.2 × 10 <sup>-12</sup>	17
13.	N <sub>2</sub> (B) <sub>v=3</sub> + N <sub>2</sub> → N <sub>2</sub> (?) + N <sub>2</sub>	2.5 × 10 <sup>-11</sup>	18
14.	N <sub>2</sub> (A) <sub>v=0</sub> + C <sub>2</sub> H <sub>6</sub> → N <sub>2</sub> + C <sub>2</sub> H <sub>6</sub> <sup>1</sup>	2.9 × 10 <sup>-13</sup>	19
15.	N <sub>2</sub> (A) <sub>v=3</sub> + C <sub>2</sub> H <sub>6</sub> → N <sub>2</sub> (A) <sub>v≤3</sub> + C <sub>2</sub> H <sub>6</sub>	1.1 × 10 <sup>-11</sup>	19

rates for B and C state formation, not to the rates for formation of specific vibrational levels. The results of Setser, et al., (Ref. 14) show that the population of  $N_2(B^3\pi_g)v = 3$  resulting from  $Ar(^3P_{0,2})$  excitation transfer is more than 15 times less than the population of  $N_2(B^3\pi_g)v = 0$ . Thus, it still may be possible to obtain an inversion on the  $C \rightarrow B(0,3)$  transition utilizing  $Ar^*$  excitation transfer as the pumping mechanism.

#### 4.3. Effect of $SF_6$

At high discharge current densities, the discharge was found to increase the  $N_2(B)$  state emission much more rapidly than the C state emission. However, the addition of small concentrations of  $SF_6$  ( $\sim 0.1\%$ ) to the gas mixture increases the ratio of the second positive emission to the first positive emission by an order of magnitude even though the discharge current decreases substantially. The onset of arc formation limited the maximum obtainable  $E/N$  to a value of  $1.3 \times 10^{-16} \text{ V-cm}^2$  for an 85/15  $Ar/N_2$  gas mixture at 200 torr total pressure. However, the addition of approximately 0.1%  $SF_6$  to the gas mixture allowed us to achieve an  $E/N$  of  $2.1 \times 10^{-16} \text{ V-cm}^2$  before arc formation occurred.

The effect of  $SF_6$  addition on the discharge voltage, discharge current, and  $3370 \text{ \AA}$  emission is shown in Figure 17. This photograph should be compared with the oscilloscope traces of Figure 14, which were obtained without  $SF_6$  added to the gas mixture. The discharge  $E/N$  in Figure 17 is approximately double that in the shot without  $SF_6$ , while the discharge current is about an order of magnitude less in the

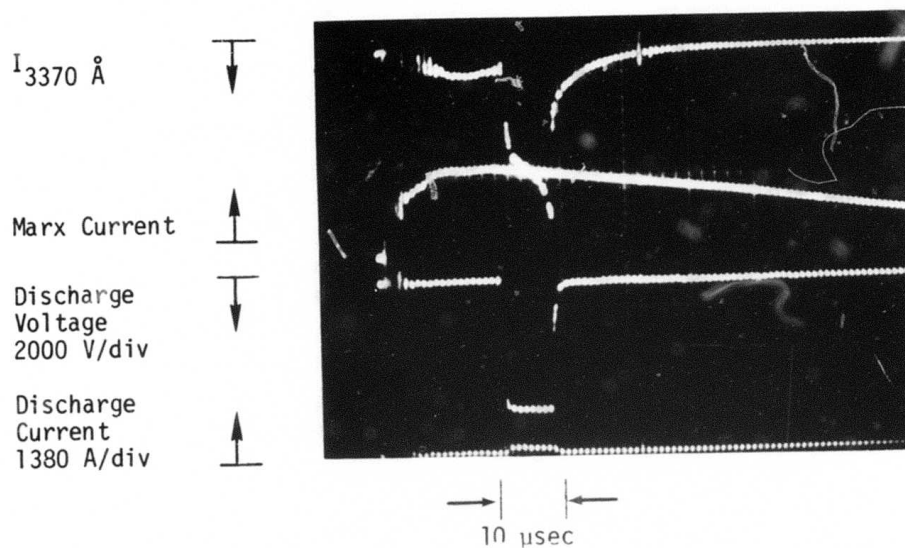
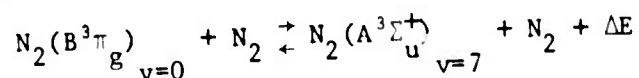


Figure 17. Effect of Approximately 0.1%  $\text{SF}_6$  Addition on the Discharge Voltage, Discharge Current, and 3370 Å Emission for an 85/15 Ar/ $\text{N}_2$  Mixture

SF<sub>6</sub> case. However, the ratio of the intensity of the 3370 Å emission produced by the discharge to that produced by the e-beam has increased substantially. The abrupt increase of the C → B emission when the discharge voltage is turned on is due to direct electron impact excitation of the C state. The emission then increases non-linearly during the discharge most likely because of the increase in the A state density which populates the C state via the energy pooling reaction. When the discharge is terminated, the second positive emission drops abruptly due to the cessation of electron impact excitation. However, there is still a slowly decaying component to the C state emission after the discharge is turned off. This component is produced by self collisions of the slowly decaying A state population.

#### 4.4. Vibrational Quenching of Lower Level

In our previous report we suggested a collisional decay mechanism for the N<sub>2</sub>(B) state utilizing ethane (C<sub>2</sub>H<sub>6</sub>). This mechanism involved an intersystem crossing from the lower vibrational levels of the B state to the upper vibrational levels of the A state



The rate constant for the formation of N<sub>2</sub>(A)v = 7 reported by Dreyer and Perner (Ref. 19) is  $\sim 1 \times 10^{-11}$  cm<sup>3</sup>/sec. The N<sub>2</sub>(A)v = 7 then decays somewhat more slowly down its own vibrational ladder until a bottleneck at the v = 3 and 4 levels is reached. The addition of small concentrations of C<sub>2</sub>H<sub>6</sub> increases the rate of decay down the A state vibrational ladder and removes the bottleneck at the v=3 and 4 levels without having a significant effect on the A state electronic energy (see Ref.19).

These ideas were tested by observing the  $3371 \text{ \AA}$  and  $1 \mu$  fluorescence with varying concentrations of  $\text{C}_2\text{H}_6$  as a function of discharge  $E/N$ . However, the addition of  $\text{C}_2\text{H}_6$  did not alter the ratio of second positive to first positive emission. The only observable effect due to the addition of  $\text{C}_2\text{H}_6$  was the disappearance of the long time decay of both the  $3371 \text{ \AA}$  and  $1 \mu$  emission. The apparent implication of this observation is that  $\text{C}_2\text{H}_6$  removes the A state; however, for the  $\text{C}_2\text{H}_6$  concentrations used here, this would be inconsistent with the rate constant for electronic quenching of  $\text{N}_2(\text{A})$  reported by Dreyer and Perner (Ref. 19). One explanation for this inconsistency is that the long time decay component of the first and second positive emission may be formed primarily by energy pooling of A state molecules in higher vibrational levels, which are quenched rapidly by  $\text{C}_2\text{H}_6$ . A second explanation is the formation of other species from  $\text{C}_2\text{H}_6$  in the discharge, which have a high  $\text{N}_2(\text{A})$  state quenching rate.

A re-evaluation of the work of Dreyer and Perner revealed an alternate interpretation for the formation of  $\text{N}_2(\text{A})v = 7$  that is also consistent with their data. The assumption is that the intersystem crossing between the B and A states takes place from the  $v = 3$  level of the B state rather than the  $v = 0$  level. This explanation is also indicated by the factor of ten larger rate coefficient for quenching of the  $\text{N}_2(\text{B}^3\pi_g) v = 3$  level by ground state  $\text{N}_2$  than for the  $\text{N}_2(\text{B}^3\pi_g)v=0,1$ , and 2 levels (Ref.18). In fact, the rate constant quoted by Dreyer and Perner (Ref. 19) for formation of the  $\text{N}_2(\text{A}^3\Sigma_u^+)v = 7$  level ( $9 \times 10^{-12} \text{ cm}^3/\text{sec}$ ) from  $\text{N}_2^*$  is in better agreement with the  $\text{N}_2$  quenching rate constant for the  $v = 3$  level of the B state ( $2.5 \times 10^{-11} \text{ cm}^3/\text{sec}$ )(Ref.18) than for the

quenching of the  $v = 0$  level of the B state ( $1.6 \times 10^{-12}$  cm<sup>3</sup>/sec) (Ref. 17). As a result of this analysis, we now feel that the best candidate for a long pulse C  $\rightarrow$  B laser is the (0,3) band at 4058 Å.

#### 4.5. Laser Cavity Measurements

In an effort to reproduce the superfluorescent emission pulses previously observed in Ar/N<sub>2</sub>/HF mixtures for both the first and second positive bands of N<sub>2</sub> (Ref. 4), we searched for laser emission at both 1  $\mu$  and 3371 Å when the discharge chamber was placed in a high-Q cavity formed from gold coated spherical mirrors. Even though an E/N of  $1.5 \times 10^{-16}$  V - cm<sup>2</sup> was reached for 89% Ar/10% N<sub>2</sub>/1% HF mixtures at 200 torr, no superfluorescent pulses were observed. At present we have no explanation for why we cannot duplicate on our present apparatus the superfluorescent pulses obtained in the old apparatus. One difference between the two experiments is that the e-beam is not crowbarred in the present set up. However, shortening the e-beam pulse by lowering the resistance of a bleeder resistor in parallel with the plasma diode had no significant effect on the first and second positive emission.

Another factor which could conceivably be responsible for the differing results is the size of the discharge volume. In the old apparatus it was 10 cm x 10 cm x 10 cm, and in the present one it is 2.5 cm x 5 cm x 50 cm, which leads us to suspect that radiation trapping (which would be affected by the size of the discharge volume) may have played a role in obtaining the superfluorescent pulses.

High-Q cavity tests using gold coated mirrors and monitoring the 3371 Å emission were made with 85% Ar/15% N<sub>2</sub> gas mixtures both with and without the addition of  $\sim 0.1\%$  SF<sub>6</sub>. With the addition of

$\text{SF}_6$  an  $E/N \sim 1.8 \times 10^{-16} \text{ V-cm}^2$  was achieved but no lasing was detected. Mixtures of 85% He/15%  $\text{N}_2$  with and without the addition of small concentrations of  $\text{SF}_6$  or  $\text{C}_2\text{H}_6$  were also tested in a high-Q cavity using dielectric coated mirrors having maximum reflectivity at  $3370 \text{ \AA}$ . Again an  $E/N \sim 1.8 \times 10^{-16} \text{ V-cm}^2$  was achieved, but no optical gain was detected.

Cavity measurements were also conducted with dielectric coated mirrors covering the range from  $3500 \text{ \AA} - 3800 \text{ \AA}$ . This range includes the  $\text{C} \rightarrow \text{B}$  (0, 1), (0, 2), and (1, 3) bands. Mixtures containing  $\text{He/N}_2/\text{SF}_6$  and  $\text{Ar/N}_2/\text{SF}_6$  at a total pressure of 200 torr were employed. The composition of the mixtures tried and the maximum  $E/N$  achieved without arcing are listed below:

<u>Composition</u>	<u>Maximum <math>E/N (\times 10^{16} \text{ V-cm}^2)</math></u>
69.9% He/30% $\text{N}_2$ /0.1% $\text{SF}_6$	3.0
89.9% He/10% $\text{N}_2$ /0.1% $\text{SF}_6$	1.7
89.9% Ar/10% $\text{N}_2$ /0.1% $\text{SF}_6$	1.7
94.9% Ar/5% $\text{N}_2$ /0.1% $\text{SF}_6$	1.4

No laser emission was detected for any of these mixtures.

#### 4.6. Conclusions

The nitrogen B and C states are populated by four mechanisms in the electric discharge: 1) direct electron impact, 2) electron impact with metastable  $\text{N}_2$  molecules or with excited vibrational levels of the ground state; 3) metastable-metastable collisions of A state molecules; and 4)  $\text{Ar}^*$  excitation transfer. Metastable-metastable collisions populate the B state more rapidly than the C state. Excitation transfer from metastable  $\text{Ar}(^3\text{P}_{0,2})$  may create a population inversion on the  $\text{C} \rightarrow \text{B}(0,3)$  transition.

At high current density, the discharge increases the B state population more rapidly than the C state. Addition of  $\text{SF}_6$  tends to stabilize the discharge and increases the ratio of the C to B state emission by an order of magnitude.

Arc formation limits the time during which the high voltage needed to populate the C state can be sustained. The onset of the glow to arc transition needs further experimental and theoretical study to determine the limits it places on electric discharge excitation of electronic states.

A search for laser emission on the  $0 \rightarrow 0(3371 \text{ \AA})$ ,  $0 \rightarrow 1(3577 \text{ \AA})$ ,  $0 \rightarrow 2(3804 \text{ \AA})$ , and  $1 \rightarrow 3(3755 \text{ \AA})$  transitions of the second positive system and the  $0 \rightarrow 0$  band of the first positive system was carried out in a high-Q cavity over a range of conditions and gas mixtures. No laser emission was found.

Further review of possible laser mechanisms indicates that the most feasible approach for making a long pulse laser is to utilize electron impact or  $\text{Ar}^*$  excitation transfer pumping of the C state and collisional quenching of the upper vibrational levels of the B state. A promising candidate for an inversion on the  $C \rightarrow B$  transition is the (0,3) band. This is due to an unusually high collisional removal mechanism for the  $v = 3$  level of the B state by ground state  $\text{N}_2$ .



## APPENDIX A

### PLASMA DIODE CURRENT PROFILES

As pointed out in earlier reports (Refs. 1 and 4), regions of weak HF excitation may lead to absorption coefficients nearly equal to the gain in adjacent regions of a non-uniform discharge. Electron beam current density measurements were made to ascertain the severity of the problem with a five element ( $1\text{ cm}^2$  each) Faraday cup array at several vertical positions below the discharge screen cathode. The Faraday cup array could also be moved horizontally along the 50 cm path inside the discharge chamber. The discharge chamber was filled with 90 torr of  $\text{SF}_6$  for these experiments.  $\text{SF}_6$  has a large electron attachment capability and captures unwanted secondary electrons. In the presence of  $\text{SF}_6$  low energy electrons produced in the discharge chamber therefore have a minimum effect on the Faraday cup measurement of high energy electrons.

Figure 18 shows centerline electron beam current density versus distance along the 50 cm horizontal path. The vertical position, 2.3 cm below the discharge cathode screen, is the approximate normal location of the 5 cm x 50 cm discharge anode. Raising the Faraday cup until it is 1.3 cm from the discharge screen increases the peak current density by 40% with little effect on the minimum current density measured between the diode tubes. The large nonuniformities in the electron beam current density profile shown here limit the laser performance that can be achieved, and also cloud the interpretation of the absorption measurements used to obtain information on the excited state populations. A uniform plasma diode gun, 50-cm long, is currently under construction.

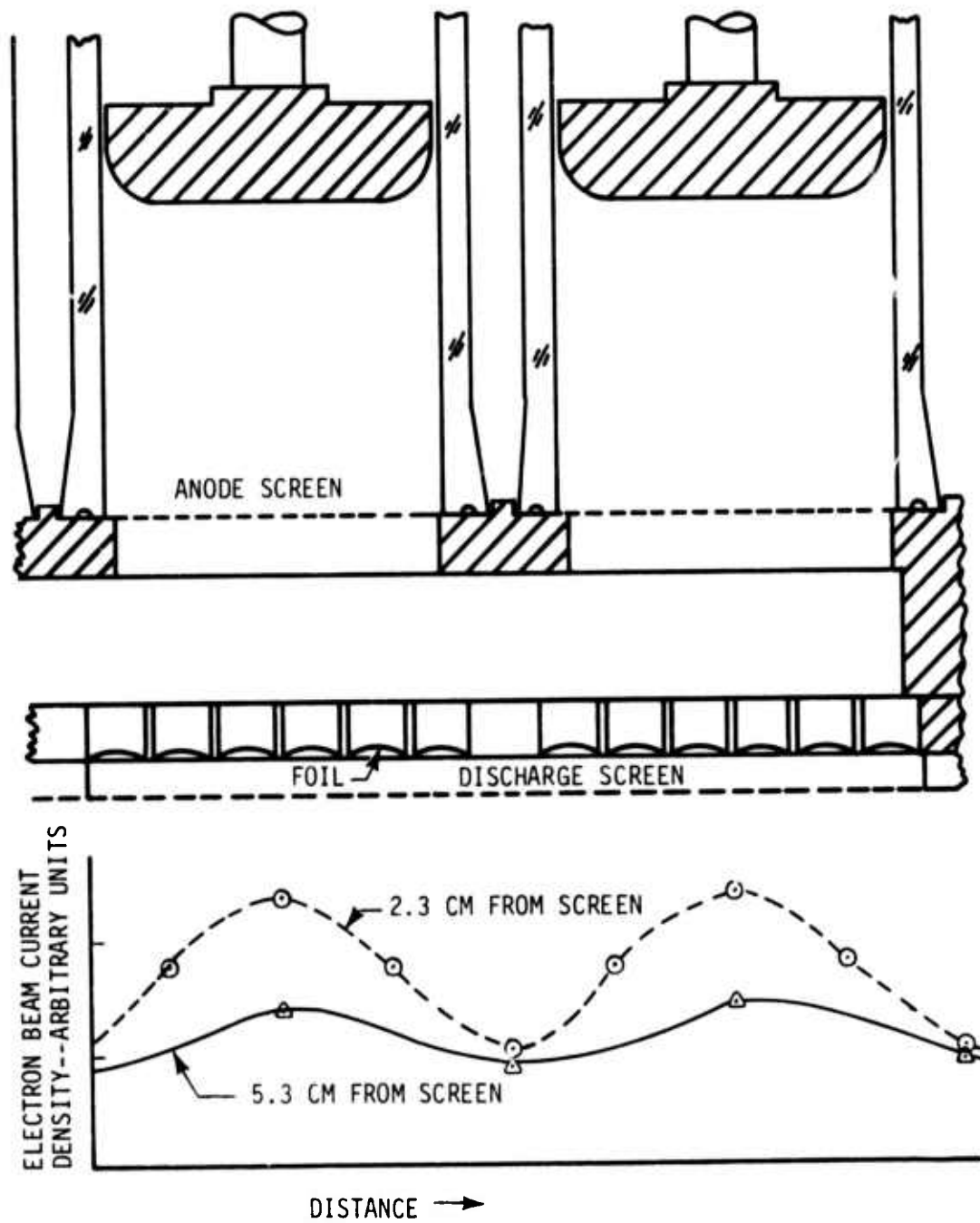


Figure 18. Electron Beam Nonuniformities Measured Below the Foil and Screen of the 5-Tube Plasma Diode Electron Gun

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